A TREATISE
ON
QUALITATIVE ANALYSIS

ADAPTED FOR USE IN THE LABORATORIES OF
COLLEGES AND TECHNICAL INSTITUTES

By

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PREFACE

THE aim of this laboratory textbook is to give all the necessary working directions so simply and fully as to reduce to a minimum the necessity of tutorial assistance.

The dimensions of the book have at the same time been kept within reasonable limits by omitting all matter which does not directly bear upon analytical work, and by avoiding lengthy theoretical explanations.

The analytical reactions and methods which are described have been carefully selected; and as they have been frequently worked through from the text by the members of our classes, their accuracy and intelligibility are, we believe, assured.

As a rule the analytical methods have been selected on account of their simplicity and the rapidity and ease of their execution. But occasionally preference has been given to methods which are delicate and trustworthy rather than rapid and simple, and the simpler methods are only recommended as substitutes for these when minute quantities of substance have not to be detected.

It has also been thought advisable to select reactions which are useful in analysis, in preference to those which claim only to be interesting or instructive; and we have not hesitated to adopt methods which are unsuitable for quantitative analysis, if they are rapid and accurate for qualitative purposes.

A glance at the contents on pages vii–xv will show that the book is divided into four main parts and that these are subdivided into eight sections.

Part I deals with the apparatus and operations which are employed in qualitative analysis.

Part II describes the analytical reactions which are used for the detection of substances, and the methods of applying these reactions.

Part III sets out the procedure for systematically employing these reactions for the detection of the composition of substances, and includes the usual analytical tables.

PREFACE

Part IV contains suggestions for fitting and furnishing the laboratory, together with full lists of the apparatus, reagents and chemicals which are required for analytical work.

The construction and use of the general apparatus required in the laboratory are also described; and suitable methods for preparing solutions of the requisite strength are set out, with the object of securing economy in time and expense. Tables of atomic weights, and of metric and English weights and measures follow at the end of this part.

The arrangement of all the tabular matter *across* instead of *along* the page will be found convenient, since it renders unnecessary the turning of the book when the table is being consulted.

Symbolic notation has been freely employed, but any perplexity to beginners which might arise from this source has been avoided by attaching the name of the substance to its symbol or formula, when this is used for the first time in the text. Both names and formulae are also associated in the tables in the eighth section, and it is recommended to have both the name and the chemical formula printed on every bottle-label in the laboratory.

Our acknowledgments for valuable suggestions are due to experienced teachers, and we have found Atack's *Chemist's Year-Book* most useful in furnishing the many recent chemical and physical constants which appear in the text.

The present edition has been rewritten, recast and enlarged in order to adapt it to modern methods of teaching. The reactions of the metals have been rearranged and placed in the natural order of the metal groups; and among the additions which have been made are the statement of the properties of metals, and many reactions, mainly for organic substances and the rarer elements: while the introduction of the modern system of standard strengths of the laboratory solutions will be found convenient. The book is presented in an altered style and size of page which makes it a companion volume to the later editions of our *Quantitative Analysis*.

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2 Porcelain dishes.
2 Watch-glasses.
1 Four-ounce (120 c.c.) c
1 Pestle and mortar.
1 Iron tripod-stand.
1 Piece of coarse iron wire-gauze.
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3 Small beakers.
3 Glass rods (15).
1 Piece of platinum-foil.
2 Pieces of platinum-wire (14).
1 Mouth-blowpipe (11).
1 Pipe-clay triangle (fig. 81, 1308).
1 Wash-bottle (17).
1 Retort-stand.
1 Wooden filter-stand (fig. 50, 43).
1 Pair of brass crucible tongs.
1 Small horn or vulcanite spatula.
1 Wicker draining-basket (21).

A fuller description of this apparatus will be found in paragraph 1368. Most of the apparatus may be seen on the bench in Fig. 82 (1360). The reference numbers in brackets refer to paragraphs in which the apparatus is described.

PART I

APPARATUS AND OPERATIONS

SECTION

DIRECTIONS FOR THE PREPARATION AND USE OF APPARATUS

1. General Remarks.—A student who is commencing work in a general laboratory will find on the preceding page and in par. 1368 a list of the apparatus which should be contained in his private locker. This apparatus should be looked through, fitted, and cleansed, as is directed in this Section.

In Section VIII. (1369 *et seq.*) will be found particulars of other apparatus, which may be used by many students in common; also lists of the various reagents, and the methods of preparing them.

For convenience in reference, paragraph numbers are printed in the text in black type, and in square brackets at the top of each

FLAMES FOR HEATING.

2. The Bunsen-burner (Fig. 1) is generally employed in the laboratory for heating purposes. It is so constructed that coal-gas, entering near its base, is mixed with a proper proportion of air before it is burnt.

FIG. 1.
BUNSEN-BURNER.

The air is drawn in through holes at the lower part of the burner, and the mixture of gas and air is burnt at the top of the upright tube. The oxygen of the air, which is thus mixed with the gas, burns the carbon in the body of the flame. Accordingly the luminosity, which depends upon the existence in the flame of unburnt carbon or carbon compounds, is destroyed.

The Bunsen-flame is therefore mainly useful because it deposits no particles of soot when it is in contact with any surface. Its high temperature and non-luminosity also render it very valuable for producing flame-colorations.

The burner should be provided with some means for partly or entirely closing the air-holes when requisite. This is usually effected by turning round a loose perforated ring outside the holes. If the flame is reduced to small dimensions, the supply of air should be partly shut off, else the flame is apt to recede.

When the burner is to be used, it is connected by means of a piece of tightly-fitting rubber tubing, about 5-16ths of an inch (7·5 mm.) in internal diameter, with the tube which supplies gas to the working-bench. The tap is then turned on, and in a few seconds the gas is lighted. The flame should be almost perfectly colourless and non-luminous.

Occasionally the gas will "burn below," that is, at the bottom instead of at the top of the burner. This usually happens when the flame is small and the quantity of air admitted through the holes is too great. It also occurs when the burner is lighted too soon after turning on the gas-supply. A luminous flame may then be seen through the holes near the base of the burner, burning from the small gas-jet inside. The flame at the top of the burner will also be long and somewhat luminous, and will emit a very unpleasant smell, which is due to the incomplete combustion of the gas.

In such a case the flame should be at once extinguished by pinching the rubber tubing close to the burner, and the gas should be relighted after it has escaped for a few seconds.

The above statements should be proved by trial, and the effect of partially or entirely closing the air-holes of the burner should be observed.

The Rose-top (Fig. 1 *a*) is employed for diffusing the heat of the flame over a large surface. It is a small perforated metal cap which is placed upon the top of the burner, and yields a circle of flames. The rose-top is put on the burner and removed from it by means of crucible-tongs. It is of course very hot after being used, and should never be handled, or placed upon wood or glass, until it is cool.

3. **High Temperature Burners** of several forms are in use for special purposes. The Fletcher and Méker burners are arranged to mix the gas and air in such proportions as to produce a "solid flame" when the mixture is burnt. The temperature in all parts of such a flame is the same and is relatively high. These flames may therefore be substituted for the blowpipe flame (PI) for many purposes.

FIG. 2.

FLETCHER BURNER.

A convenient form of Argand Fletcher-burner for supporting and heating large vessels is shown in Fig. 2; its flame is compact, and in regulating the size of the flame the proportion of gas to air is automatically adjusted.

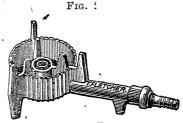
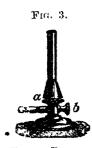



FIG. 3.

TECLU BURNER.

The Teclu Burner (Fig. 3) is a suitable high temperature burner for use on the working-bench. In this burner the air enters through the conical part and its supply is regulated by rotating the disc (*a*), and the gas-feed is regulated by the rotation of the screw (*b*). When the highest temperature is required, the full supply of gas is turned on, and the disc is rotated until a roaring flame is produced.

4. **Other Special Burners** (5, 6, 7) are occasionally used instead of gas-burners; but for general purposes they should only replace the gas-burners when coal-gas cannot be obtained.

5. **The Spirit-lamp** (Fig. 4) consists of a glass vessel containing methylated spirit, into which dips a cotton wick supported by means of a brass or stoneware wick-holder.

When the lamp is not in use the upper end of the wick should always be covered with the glass cap, in order to prevent evaporation of the spirit.

If the spirit is tolerably free from resinous matter, its flame will be non-luminous and will deposit no soot.

6. **Vapour Burners**, arranged to burn a mixture of air with vaporised methylated spirit or petroleum, are now obtainable, and may be used in laboratories where a supply of coal-gas is not available.

FIG. 4.

SPIRIT-LAMP.

A burner similar in form to the Bunsen-burner (2) for burning a mixture of vaporised methylated spirit with air, and a metal lamp which furnishes a smokeless non-luminous flame with vaporised petroleum oil, are described in paragraph 1366.

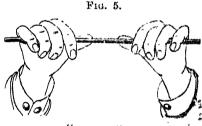
7. **An Acetylene Bunsen-burner** may also be used, the acetylene gas being made as required in an automatic apparatus by the action of water on calcium carbide, or a supply of the gas being stored in a small gas-holder.

Such a burner can be used in laboratories which are situated at a distance from gas-works, and a laboratory attendant can easily perform the duties of gas-maker if the gas is stored.

CUTTING AND BENDING GLASS TUBE AND ROD.

8. **Glass Tube or Rod is Cut** by laying it upon a flat surface, and making a deep scratch with the edge of a three-cornered file at the point to be cut. The glass is then held with both hands, one on each side of the scratch and close to it, and a gentle pressure is exerted upon the glass as if trying to break it across (Fig. 5). If the file-mark has been made sufficiently deep, the glass will readily break at this point.

The sharp edges of a freshly-cut rod or tube should always be at once rounded. This is effected either by holding the end of the tube in the Bunsen-flame or blowpipe-flame until the edges are partly melted (Fig. 8, page 6), or by rubbing off the sharp edge with the face of a file.

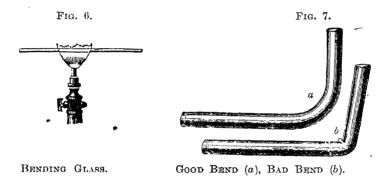
FIG. 5.

CUTTING GLASS.

Select a length of glass tubing, which is about one-eighth of an inch (3 mm.) in internal diameter. Cut from it one piece about ten inches (25 cm.) and two pieces about five inches (12·5 cm.) long, and carefully round off their sharp freshly-cut edges. Also cut off three pieces of glass rod, respectively seven, six, and three inches (18, 15, and 7·5 cm.) in length. Keep these for future use.

9. Ordinary Glass Tube is Bent by holding it in the upper edge of a common fish-tail gas-flame, so as to heat at least two inches of the glass (Fig. 6). The tube is supported by both hands, one on either side of the flame, and is constantly turned slowly round on its axis, in order to heat all sides equally. As soon as the glass is felt to be soft and pliable, it is taken out of the flame and is at once quickly bent to the required angle. The heated part must not be allowed to touch anything until it is cold. The soot is then removed from it by a cloth or by a piece of paper.

If a bend is properly made, it should be a curve and should not alter the bore of the tube (Fig. 7 *a*). If a sharp angle is made,

FIG. 6. FIG. 7.

BENDING GLASS. GOOD BEND (*a*), BAD BEND (*b*).

the bore will be narrowed (Fig. 7 *b*), and the bend will not only be unsightly, but weak and liable to break under a small strain.

Bend the longest piece of glass tubing (8) at right angles, so that the shorter part is about two inches (5 cm.) in length. Keep this for future use.

10. Glass rod, Hard glass tube, and Tube with Thick Walls or Small Bore may be bent in the Bunsen-flame, or even in hotter flames including the blowpipe-flame. But these flames are not suitable in shape for bending ordinary glass tube, as they soften the walls too much and cause it to get out of shape.

THE BLOWPIPE, AND ITS USE.

11. The Mouth blowpipe is used for producing a small but very hot flame, which can be made to assume any desired direction. This is effected by blowing a fine stream of air from the mouth through a gas-flame.

The blowpipe is held in the right hand, with its finely pierced tip resting on the edge of the burner, and just inside the flame

(Fig. 8). The mouthpiece is then taken between the lips; and after the cheeks have been blown out to their full extent, the air contained in them is forced out through the jet. This produces a small pointed conical flame in the direction of the blast.

The chief difficulty in using the blowpipe properly is experienced in maintaining the blast of air uninterrupted by breathing. Patient trial will, however, remove this difficulty, if it is borne in mind that the cheeks are to be kept constantly inflated with air, and that the air must be forced through the blowpipe by the muscles of the cheeks, and not by the action of the lungs, breathing being meanwhile carried on through the nose, and the mouth being occasionally rapidly replenished from the lungs.

FIG. 8. FIG. 9.

ROUNDING THE END.

DRAWING OFF GLASS.

It is frequently necessary to have both hands free while the blowpipe is being used. This may be secured by resting the blowpipe-jet upon the top of the gas-burner and supporting the mouthpiece by the lips alone, as is shown in Fig. 9.

A small flame, made luminous by nearly closing the air-holes of the Bunsen-burner, is better suited for most blowpipe-work than the ordinary non-luminous flame of the burner.

It is important that the hole in the nozzle of the blowpipe should be small and round, else a good flame will not be obtained; and unless the hole is very small it will be found difficult to maintain a continuous blast.

The student should, as soon as possible, acquire dexterity in the use of the mouth-blowpipe, since its flame serves for many of the shorter heating processes of the chemical laboratory.

12. A Blast blowpipe (Fig. 10) which is fed with air from the foot-bellows (Fig. 11), or from a mechanical or water blower, is often advantageously employed for maintaining a high temperature in fusion processes, or for extensive glass-working or glass-blowing.

The special form of Bunsen-blowpipe shown in Fig. 10 is suitable for many purposes. It consists of a somewhat large Bunsen-burner (2), which is furnished with two taps. One of

FIG. 10.

BUNSEN-BLOWPIPE.

FIG. 11.

FOOT-BELLOWS.

these taps controls the gas-supply, and the other controls the air blast from the bellows.

When a Bunsen-flame is required, the gas is supplied to the burner, and the air-supply is adjusted at the base of the burner by the ring D.

When the blowpipe-flame is to be used, the metal ring B is placed upon the top of the burner so as to reduce the aperture, and the supply of gas and the air-blast are regulated until a flame of the necessary character is obtained.

The Bunsen Gas-blowpipe (1365) will be found better adapted than the above for more elaborate glass-blowing and working.

The Herapath Gas-blowpipe (1365) is convenient for smaller heating purposes. It can, if desired, be blown by the mouth. It may be purchased without the foot and the tap, the upright tube being slipped down the tube of a Bunsen-burner.

A Petrol, or Spirit, Blowpipe (1366) may be used where coal-gas is not available. It possesses the advantage of being portable and of requiring no bellows or air-blast.

13. Small Ignition-tubes.—One of the pieces of glass tubing, about five inches (13 cm.) in length (8), is drawn out at its middle point by heating it strongly in the blowpipe-flame (Fig. 9, page 6).

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While the tube is being heated, it is held in both hands, and is constantly turned round upon its long axis in order to secure uniform heating. As soon as the glass is softened, it is gradually drawn out by pulling the ends of the tube in opposite directions. The narrowed portion of the tube (Fig. 12) is then cut across

FIG. 12.

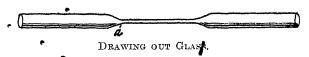
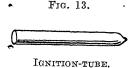
DRAWING OUT GLASS.

(8) at its middle point, the conical part (*a*) is heated in the blowpipe-flame, and the narrow portion is drawn off, producing a small closed tube (Fig. 13).

FIG. 13.

IGNITION-TUBE.

The closed end may be heated to redness in the blowpipe-flame, and expanded into a small bulb by gently blowing down the tube.

Small test-tubes, three inches (7·5 cm.) long by a quarter of an inch (6 mm.) in diameter, will also serve for ignition-tubes.

14. **Mounted Platinum Wires.**—Select a length of platinum wire about as stout as a small pin. Ascertain that the wire does not permanently impart colour to a Bunsen-flame when it is heated to bright redness in the flame. Cut off two pieces of this wire, each about two inches (5 cm.) in length, and proceed to fix them in glass handles in the following way. This will facilitate their being held in the fingers, and will help to prevent them from being lost.

Draw out at its middle point (Fig. 12,) the piece of glass tube (8) about five inches (13 cm.) in length, and cut it across at the middle of the narrow portion. Each of the pieces of tube thus obtained serves for the handle of a wire.

Break off the narrow part of the tube until it extends only about a quarter of an inch (6 mm.) from the shoulder, *a* (Fig. 12). Insert the end of the platinum wire into this narrow opening. Then hold

FIG. 14.

MOUNTED PLATINUM WIRE.

the end of the tube, containing the wire, in the blowpipe flame, until the glass melts and thickens around the end of the wire, fixing it firmly when cold (Fig. 14).

The free end of the wire may then be rolled round a stout wire into a loop about an eighth of an inch (3 mm.) across.

15. Glass Stirring-rods.—Remove by a file any small projections from the ends of each of the glass-rods, which were made (8) by cutting some solid glass-rod into lengths of about three, six, and seven inches (7·5, 15 and 18 cm.). Then heat both ends of each rod to redness in the tip of the blowpipe-flame, the rod being meanwhile constantly turned round on its long axis (Fig. 8, page 6). The sharp edges of the glass are thus rounded by fusion. The end of the rod must not be allowed to touch anything until it is cool.

Sometimes a very slender rod is required. This may be obtained by heating a suitable point in an ordinary glass rod with constant rotation in the blowpipe-flame until the glass is well softened, and then drawing it out to the requisite fineness. See Fig. 9 (page 6) and Fig. 12.

BORING CORKS.

16. A Cork may be Bored, for the insertion of a glass tube, by gradually pushing through it a sharply pointed and slender round file with a constant twisting movement, and then enlarging the hole with the file to the necessary size.

The Cork-borer, which is a brass tube sharpened at one end, is, however, more commonly used.

A borer must be selected which is rather less in size than the glass tube which is to be inserted into the cork. The cork is then pressed against a wooden surface or grasped firmly in the hand, and the perforation is made by gently pushing the borer through it with a constant movement of rotation backwards and forwards upon its axis (Fig. 15). Caution and practice will enable the student to make a clean straight hole without damaging the surrounding parts of the cork.

FIG. 15.

BORING A CORK.

In making a single central hole through a cork, it is well to bore from the centre of one end of the cork half-way towards the other end, and then reverse the cork and bore a hole to meet this from

the centre of the opposite end. In this way a hole which is central in position throughout the cork is most easily obtained.

A slender round file is used for smoothing the sides of a hole which has been made by a cork-borer, or for slightly enlarging it. Great care must be taken to leave the hole round in shape, and not to enlarge it so much that the glass tube fits loosely.

The cutting edge of the cork-borer is sharpened by rubbing its inner surface with a round file, and then rubbing the outer surface obliquely with the face of a flat or triangular file.

Rubber Corks are perforated in a similar manner by a sharp borer which is either partly filled with water, or is moistened with alcohol or glycerine.

FITTING THE WASH-BOTTLE.

17. **The Wash-bottle.**—A thin, flat-bottomed, conical flask, about eighteen ounces (500 c.c.) in capacity, and not less than an inch (2·5 cm.) in diameter in the neck, should be fitted as is shown in Fig. 16.

FIG. 16.

THE WASH-BOTTLE.

For this purpose a sound cork is selected which is slightly too large to enter the neck of the flask. The cork is softened by rolling it backwards and forwards under the foot with gentle pressure ; it must now fit tightly into the neck of the flask.

Two pieces of glass tubing, rather longer than the tubes (*a*, *b*), are then bent (9) into the form shown in Fig. 16. Their ends are cut off to the right length, and the sharp edges are rounded by holding them in the Bunsen-flame, or by rubbing them with the face of the file.

Two parallel holes are then bored through the cork, with a proper sized cork-borer (16) or by means of a round file. The holes must be somewhat smaller than the glass tubes, and must not run into one another or to the outside of the cork. They are smoothed, and slightly enlarged if necessary, by means of the round file.

Into these holes the tubes (*a*, *b*) are then gently pushed with a twisting motion. They must enter somewhat stiffly, but without requiring much pressure. If the holes have been carelessly made too large, the tubes may often be made to fit by slipping upon them little pieces of wetted narrow rubber tubing, or by putting the

wetted pieces of rubber tubing into the holes in the cork before the glass tubes are pushed in.

A Rubber Cork is much more durable than an ordinary cork for this and for most other chemical purposes. It may be purchased with two holes already made, or may be perforated by a sharp well-wetted cork-borer (16), or by a wetted round file. Both the glass tubes and the inside of the holes should be wetted before the tubes are pushed in, since water serves as a lubricant for glass against rubber.

Before the further fitting of the wash-bottle is proceeded with, the cork with the tubes is inserted into the neck of the flask. One tube is then closed with the finger, and air is blown through the other tube into the flask, so as to produce pressure in its interior. The cork is meanwhile carefully watched in order to ascertain whether there is any escape of air. A leakage is as a rule easily heard: but if the outside of the cork is wetted with water, any escape of air-bubbles will be readily seen.

If the cork is air-tight, a piece of rubber tubing, about an inch (2·5 cm.) in length, is pushed upon the upper end of the tube (*a*). A short jet (*c*), which has been made by drawing out a piece of glass tubing in the flame (Figs. 9, 12, pages 6, 8), is fitted into the other end of the rubber tube. The narrow opening of the glass jet may be further contracted, if necessary, by holding it in the flame for a short time and slightly fusing the edges of the glass.

If the wash-bottle is to be heated, the neck of the flask should now be bound round with twine like the handle of a cricket bat, or tightly covered with a folded strip of flannel. The neck, when thus protected, can be grasped with comfort even after water has been boiled in the flask and the neck has become heated by steam.

The wash-bottle is now filled about two-thirds with distilled water, and is ready for use. Tap-water should never be kept in the wash-bottle.

A fine stream of water may be obtained from the jet (*c*), by blowing down the tube (*b*).

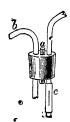
This stream serves for washing precipitates and for other purposes. A larger stream may be obtained by inverting the flask, when the water will flow out from the end of the tube (*b*), air entering meanwhile by the tube (*a*): this stream can be made to issue with greater force and speed by blowing down the tube (*a*).

When hot water is required, the wash-bottle is supported on a tripod-stand upon a piece of coarse iron-wire gauze, and is heated by the Bunsen-flame: or it may be heated by the small Fletcher-burner (Fig. 2, page 3).

18. **When Boiling Water, or a Liquid which gives off Vapour or Gas,**

is used in the wash-bottle, a special stopper, shown in Fig. 17, should be fitted into the neck of the bottle, in order to prevent the vapour or gas from entering the mouth.

The stopper is perforated with three holes. Through the centre hole is pushed a short glass tube (*a*), which terminates just above and just below the stopper.

FIG. 17.

FITTING FOR HOT-WATER BOTTLE.

The other holes carry the jet-tube, the upper part of which is shown (*b*), and the blow-tube (*c*), as in the ordinary wash-bottle. The lower end of the blow-tube, however, is fitted with a valve, which is formed by slipping over it, a piece of rubber tube with a slit cut in it (*c*) and which is closed below by a piece of glass rod.

While the wash-bottle is being used the tube (*a*) is closed with the finger, and air is blown in through the valve (*c*). The valve prevents the air from returning through the blow-tube and introducing vapour or gas into the mouth. When the stream is to be stopped, the finger is removed from the tube (*a*) and the pressure of air in the interior of the flask is released.

CLEANING APPARATUS.

It is indispensable that all glass and porcelain apparatus should be kept scrupulously clean, and the student should cleanse his set of apparatus as is directed below. In ordinary work the apparatus should be cleansed before it is put away.

19. **Test-tube Brush.**—This brush is constantly in use for cleansing glass and porcelain apparatus.

The piece of sponge, which is sometimes fastened on the end of the brush (Fig. 18 *a*), does not adapt itself well to the bottom of test-tubes and boiling-tubes. A much more efficient end is given to the brush by removing the sponge and then bending back the end of the wire stem sharply upon itself at a point just above where the hairs commence (Fig. 18 *b*).

By slightly curving the part of the stem carrying hairs, the brush will better adapt itself to the curved surfaces of porcelain dishes.

FIG. 18.

TEST-TUBE CLEANER.

20. **Test-tubes, Beakers, Funnels and Porcelain-dishes** are washed in a stream of tap-water, their surfaces being rubbed meanwhile by the test-tube cleaner (Fig. 18 *b*).

The brush must be cautiously moved as it approaches the botto[m] of a test-tube or boiling-tube, since the glass is very thin, and therefore easily broken by undue pressure.

Glass funnels which are used for qualitative analysis may hav[e]

their stems cut off at about two inches from the shoulder (8), the sharp outer edge thus produced being at once removed by rubbing it with the face of a triangular file. The inside of the shortened neck can then be easily cleaned by rubbing it with a strip of wood, or by inserting an ordinary tobacco-pipe cleaner from the shoulder of the funnel so as not to cut the hairs.

Occasionally the cleaning-brush fails to remove strongly adhering stains. Rubbing with the finger-end covered with a little moistened sea-sand or powdered pumice will usually be effectual in the case of an open vessel; and in the case of a bottle or flask a little water may be shaken round inside with sand, pumice powder, saw dust or small pieces of paper.

Or the stain may be removed by a suitable solvent, or by a liquid which renders the substance of the stain soluble by chemical change.

Hot dilute hydrochloric acid will remove most stains in this way; but it is sometimes necessary to heat a little strong sulphuric or nitric acid in a vessel in order to cleanse it. Hot solution of caustic potash or of ammonia may also often be used with advantage to remove grease.

Apparatus should be washed as soon as possible after it has been used, since after the apparatus has stood aside for some time the surface is usually less easily cleansed.

Each article, after it has been carefully washed, and then rinsed out with tap-water, should be placed upside down in the small wicker-basket to drain. If it is required for immediate use for analysis and cannot be allowed to drain, it may be rinsed out with a little distilled water. This rapidly removes the tap-water which itself often contains dissolved impurities.

21. **Draining-basket.**—Before apparatus is placed in the locker, it should be made a rule to wash all glass and porcelain which is not in actual use, and then to place it in a wicker basket to drain. The basket is then put away with its contents. Dirty apparatus should never be kept in the basket.

All iron apparatus should be carefully dried, and must be kept in a dry place to prevent it from rusting.

Metal apparatus must never be put into the basket.

22. **Platinum Foil and Platinum Wire** are cleansed by boiling them in hydrochloric acid, and rinsing off the acid with water. The wire should then be strongly heated for some time in the blowpipe-flame, until, when it is wetted with pure strong hydrochloric acid and held in the Bunsen-flame, it no longer persistently colours the flame.

If the tip of the wire cannot be cleansed in this way, it should be cut off. Commercial platinum sometimes persistently colours the flame: wire made from such platinum is useless for flame-coloration tests and for spectrum analysis.

Platinum-foil and wire should be kept in a small beaker containing strong hydrochloric acid, which has been previously diluted with sufficient water to prevent it from fuming. When the platinum is removed from the acid and has been rinsed with water, it will usually be found to be clean and to give no colour to the flame.

HEATING PORCELAIN AND GLASS.

23. **A few general Precautions** should be observed in heating glass and porcelain vessels, in order to guard against cracking them. The two following rules apply to both glass and porcelain:—

A vessel containing a liquid must never be heated by the flame above the level of the liquid inside.

A hot dry vessel must be allowed to cool before any liquid is poured into it, and before it is placed upon a cold surface.

24. **Porcelain Vessels** withstand higher temperatures than glass vessels, and are not so liable to be cracked by being suddenly heated or cooled.

Porcelain Dishes are generally used for the purpose of evaporating liquids to dryness, or for concentrating them. They are supported on a pipe-clay triangle, which is placed upon a tripod-stand or a retort-stand. Porcelain dishes may be safely heated by a small naked flame.

Porcelain Crucibles are used for strongly heating solid bodies. Crucibles are supported in the same way as porcelain dishes. The flame should not be allowed to play steadily upon the bottom of the crucible so as to heat it suddenly, but the burner should be constantly moved slightly from side to side until the porcelain is hot.

The crucible should also be allowed to cool slowly on the triangle, since contact with a cold body is very apt to crack it. The hot crucible and cover are handled by the crucible-tongs.

25. **Glass Vessels require to be Heated** more cautiously than porcelain vessels. A large naked flame must never be allowed to play for any length of time on one part of the glass surface.

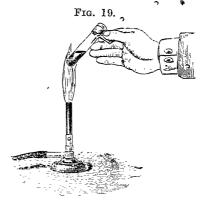
When a test-tube or boiling-tube is being heated, this *local heating* is prevented by holding the tube obliquely with the lower part in the flame, and either moving the tube slowly up and down, or shaking the contents of the tube (Fig. 19).

Test-tubes and Boiling-tubes.—Ordinary test-tubes are too narrow to contain safely a large quantity of boiling liquid, since the upper portion of the liquid is liable to be projected from the tube during ebullition. A small quantity of liquid may be boiled, and a larger quantity may be heated short of boiling, in a test-tube. But the broader "boiling-tubes" are to be preferred when a liquid is to be boiled.

Test-tubes, or boiling-tubes, which are not full of liquid, can be held by the neck while they are being heated. They should be supported in an oblique position, so that the fingers are not over the flame (Fig. 19).

FIG. 19.

HOLDER FOR TEST-TUBE.

If steam or vapour is emitted in quantity, all risk of burning the fingers is avoided by bending round the neck of the tube a strip of folded glazed paper, or of leather, and pinching the ends of the strip together close to the tube, as is shown in the figure. This simple device serves better than a metal holder.

It is dangerous to use a strip of unglazed filter-paper, since if it becomes wetted it breaks and allows the tube to fall.

Crucible-tongs must never be used for holding test-tubes.

Glass Flasks, such as the wash-bottle, are most safely heated by placing them on a piece of wire-gauze on a tripod-stand over the Bunsen-flame (2), or they may be heated over the Fletcher flame (Fig. 2, page 3). If a large sand-bath, hot plate, or water-bath (Figs. 26, 28, pages 22, 23) is available, the flask may be heated on the hot surface or by the steam.

SECTION II

ANALYTICAL OPERATIONS, ILLUSTRATED BY EXPERIMENTS

29. **Introductory Remarks.**—Before the student tries the analytical reactions, he should become familiar with the operations which are commonly employed in chemical analysis. He may obtain this knowledge by reading through the following descriptions, and then performing the illustrative experiments.

Each student should work independently.

In all analytical work the water used must be distilled water, and this is conveniently kept in the wash-bottle.

A list of the chemicals required in this section will be found in par. 1408, and lists of the apparatus in pars. 1368, 1369.

DISTILLATION, DISTILLED WATER.

30. **The Process of Distillation** is often used to purify a liquid from solid substances which it contains in solution. The process consists in boiling the liquid and cooling or "condensing" the vapour. The solid substances are left behind in the vessel in which the liquid is boiled, and the condensed vapour forms the liquid "distillate."

The purification of spring water from the salts dissolved in it will serve as an example of this process.

31. **Tests for Salts dissolved in Tap-water.**—Certain salts, which are ordinarily present in spring-water, may be tested for as is directed below. But it must be understood that all the results which are described may not be obtained, since the soft water supplies of some of our large towns are almost free from dissolved solids. Rain water, or soft water, which gives no results with these tests, may be employed in qualitative analysis without previous distillation. A sample of water which contains saline impurities must be obtained for the following tests.

EXPERIMENT 1.—Make each of the following tests on a separate portion of the water contained in a test-tube.

(*a*) *Chloride.*—Add to some of the water several drops of dilute

nitric acid and of silver nitrate solution, and notice whether the water becomes turbid. Turbidity shows the presence of chloride in the water.

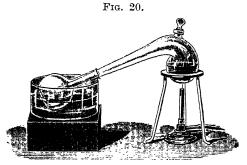
Calcium.—A separate portion of water in another test-tube may be found to become turbid on the addition of some solution of ammonia and of ammonium oxalate. Dissolved calcium salts produce this turbidity.

Sulphate.—The presence of sulphate would be indicated by a turbidity being produced on the addition to another portion of the water of a few drops of hydrochloric acid and of barium chloride solution.

Hardness.—Ascertain also whether precipitation of soap is caused by the water, owing to the presence in it of certain dissolved solids.

For this purpose dissolve a small shaving of soap by warming it in a little distilled water. Add a drop of this soap-solution to some of the water, which half fills a test-tube. Close the mouth of the test-tube with the thumb, and shake the water well.

If "hardening salts" are present no lather will form, but the water will be rendered more or less turbid by the separation of soap; but by the gradual addition of more soap-solution, the initial turbidity will be increased, and ultimately a lather will be produced when the water is shaken.

FIG. 20.

DISTILLATION OF WATER.

32. Distilled water and Tests for its Purity.—Distilled water is made in large quantities for use in various chemical processes. It must be substituted for ordinary water in the process of analysis, if the water-supply contains dissolved solids.

The student may use a glass retort and cooled flask (Fig. 20) to produce a little distilled water for the following tests, or he may use some of the distilled water supplied to the laboratory. An apparatus for preparing distilled water in larger quantity is described in paragraph 1377.

EXPERIMENT 2.—Distilled water, when it is examined by th tests described in paragraph 31, should remain perfectly clea Solution of ammonium oxalate, of silver nitrate, of barium chlorid and of ammonium sulphide when separately added to fresh portion of the water should produce no precipitate.

These tests prove the absence of calcium salts, of chloride, o sulphate, and of lead and iron salts respectively, any or all of whic have been removed by distillation. Prove also that distilled wate at once gives a lather with soap-solution, and leaves no residu when it is evaporated to dryness (37).

SOLUTION.

33. **The Process of Solution.**—Many solid substances gradually dissolve in water, when they are stirred or shaken with that liquid. Salt and alum may be mentioned as examples. Certain other liquids may be employed instead of water; and if they cause solid substances which are immersed in them to become partially or entirely liquid, and to mingle uniformly with the liquid, they are said to "dissolve" the solids.

The liquid thus obtained is called a "solution" of the solid, and the liquid which dissolves the solid is termed the "solvent."

Further, a solid which dissolves in a liquid is said to be "soluble" in that liquid; if it does not dissolve, it is said to be "insoluble."

Thus when water is shaken with sodium chloride or common salt it dissolves the salt, yielding solution of sodium chloride; water is therefore called a solvent for sodium chloride, and this salt is said to be soluble in water.

The process of solution proceeds most rapidly when the solid substance is finely powdered before it is stirred in the liquid, since the largest possible surface of the substance is thus brought into contact with the solvent.

The process is also much hastened by heating the solvent, partly because heat causes a rapid circulation of the liquid over the solid, and also because a solid substance is usually much more soluble in the hot liquid than in the cold.

Two kinds of solution may be distinguished, namely "simple solution" and "chemical solution."

34. **Simple Solution** occurs when a substance is dissolved by a liquid without undergoing permanent alteration in its composition.

A simple solution therefore generally possesses the taste, colour, and other general properties of the solid which it contains. It also yields the solid substance again when the solvent is removed by "evaporation,"

The solution of potassium nitrate or of copper sulphate in water is an example of a simple solution.

EXPERIMENT 3.—Place a small piece of potassium nitrate in a small clean beaker. Partly fill the beaker with water, and stir the solid about with a glass rod. The potassium nitrate will slowly dissolve in the water, and the solid will diminish in amount.

Now heat the liquid by placing the beaker on wire-gauze over a small flame; the solution will proceed much more rapidly.

Powder another piece of potassium nitrate by crushing it in a mortar, and then rubbing it round with the pestle. Place this powder in a beaker, pour in water, and heat the bottom of the beaker on wire-gauze by a small Bunsen-flame (Fig. 21 A, page 20). The potassium nitrate will dissolve much more rapidly than before, showing that the process of solution is accelerated by powdering the solid and by employing heat.

Mix these solutions, and preserve the liquid for future use.

EXPERIMENT 4.—Powder a little copper sulphate in a mortar, and transfer it to a small porcelain dish. Half fill the dish with water, support it upon a pipe-clay triangle placed on a tripod- or retort-stand, and heat it with a small flame. The blue copper sulphate will dissolve, yielding a blue solution. Keep this solution for future use.

These experiments (3, 4) are examples of simple solution. The first shows that a colourless solid gives a colourless solution, and the second that a coloured solid gives a coloured solution. This is generally true, and hence the presence of a coloured substance in a solution may be inferred if the liquid itself is coloured.

Moreover if a drop of the potassium nitrate solution is tasted, it will be found to possess the same taste as the solid.

Before a simple solution is analysed its colour is therefore usually noted, and its taste is occasionally tried with proper precautions.

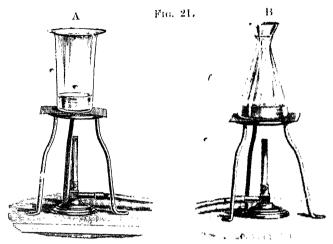
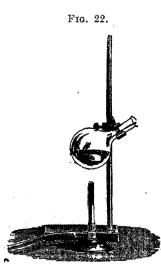
35. **Chemical Solution** differs from simple solution by producing a chemical change in the substance which is undergoing solution. The solution therefore contains a substance which differs in composition from the undissolved solid. Accordingly when the solvent is removed by evaporation the original substance is not obtained.

EXPERIMENT 5.—Place in a test-tube a small piece of marble or chalk, calcium carbonate, pour upon it a little water and heat the tube. The calcium carbonate will be found to be insoluble in water.

Now add to the water some hydrochloric acid: "effervescence," or escape of numerous small bubbles of gas, will occur. The piece

of calcium carbonate will meanwhile slowly diminish in size and will at last entirely disappear in the liquid, if sufficient acid is added.

EXPERIMENT 6.—Place in a test-tube a small piece of copper, and warm it with a little water: the copper will remain undissolved. Now add to the water some nitric acid and heat: the copper will slowly dissolve, yielding a reddish-brown gas. The metal may be entirely dissolved, if sufficient nitric acid is employed.

FIG. 21.

APPARATUS FOR DISSOLVING A SOLID.

These are two examples of chemical solution. The calcium carbonate is changed by the hydrochloric acid into calcium chloride, and this substance, not the calcium carbonate, remains in solution. The copper is changed into copper nitrate, which is then dissolved by the water. These solutions would therefore furnish on evaporation calcium chloride and copper nitrate respectively, and not marble or metallic copper.

FIG. 22.

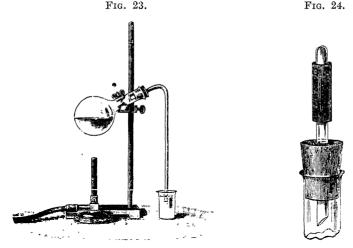
DISSOLVING A SOLID.

It will be noticed that in each of these cases a gas is given off. This is a very usual, but not a universal effect during the process of chemical solution. The distinguishing fact is that the solid substance has undergone a change in composition in the act of passing into solution.

36. Apparatus for Solution of Solids.—As will have been already seen, the apparatus used for the solution of solids may be a test-tube, a porcelain dish, a beaker or a flask.

In Figs. 21 A, B, it is shown how loss by spirting from a boiling or effervescing liquid may be prevented by a clock-glass cover or a funnel. In Fig. 22 the inclination of the flask serves the same purpose, and in Fig. 23 the spirtings are collected in a small beaker containing water, and the water may be returned to the flask. These devices also tend to check the loss of the solvent by evaporation; they are, however, not usually necessary.

It is sometimes necessary to dissolve a substance without exposing it to contact with the air during the process. This may be effected by passing a stream of carbon dioxide through the vessel in which the solution is proceeding; or the air may be displaced from the flask by carbon dioxide, and

FIG. 23. FIG. 24.

DISSOLVING A SOLID OUT OF CONTACT WITH AIR.

then a perforated cork may be at once fitted into the neck of the flask. The perforation carries either a bent tube with its end just immersed in a small quantity of distilled water (Fig. 23) forming a water valve, or a short tube surmounted by a piece of rubber tube which is closed with a solid glass stopper: the rubber tube has a slit cut in it by a sharp knife (Fig. 24), and this slit gives egress to any gas or vapour from within, but excludes the entrance of air from without.

EVAPORATION AND CRYSTALLISATION.

37. The Process of Evaporation.—When it is necessary to separate a solid substance from the liquid in which it is dissolved, the liquid is boiled away as vapour or "evaporated." The solid

substance is then left behind in the vessel. The liquid is usually removed by heating the solution in an open porcelain evaporating dish over the Bunsen-flame.

FIG. 25.

EVAPORATION IN DISH.

EXPERIMENT 7. Pour the potassium nitrate solution (Exp. 3, page 19) into a porcelain evaporating basin, and heat it over the Bunsen flame until the water has been nearly removed.

Then make the flame smaller, and continue heating until the water has disappeared. Solid potassium nitrate will be left in the dish.

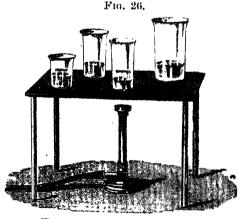
Towards the end of the process of evaporating a solution, a small flame should always be used; and in order to prevent the substance from spirting out of the dish, the flame is moved about, or the dish may be covered with a funnel (Fig. 25) or with a circular filter-paper.

The process of evaporation in a shallow dish over a naked flame is shown in Fig. 42, and the covering of the liquid during the latter stage of the process is indicated. Fig. 43 illustrates another method of evaporating on a heated iron plate, the liquid being contained in a beaker instead of in a dish; the nearer the beaker is placed to the part of the plate which is over the flame, the more rapid will be the evaporation.

38. Evaporation at Steam-heat. — It is often necessary to evaporate more slowly at steam-heat, in order to prevent the spirting of the liquid or the overheating of the solid. For this purpose the dish is placed over boiling water upon a water-bath, steam being in this case the heating agent.

FIG. 26.

EVAPORATION IN BEAKERS.

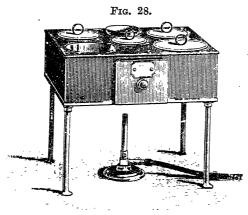
A simple form of water-bath is shown in Fig. 27. It consists of a copper vessel which is rather more than half-filled with water, and is heated by a Bunsen-burner. The

upper portion is fitted with flat sheet-copper rings of gradually diminishing diameters, and the top of the bath can thus be made to support vessels of various sizes.

A more complex form of copper water-bath is shown in Fig. 28. In the upper surface of this bath there are holes of various sizes, designed to fit vessels of different dimensions. When these holes are not in use, they are covered by lids as is shown in the figure. This form of water-bath is usually fitted with the automatic water supply represented in Fig. 41 (page 33).

FIG. 27.

SINGLE WATER-BATH.

A simple water-bath may be improvised from a beaker partly filled with water and heated by a Bunsen-flame (Fig. 29, page 24). A few small pieces of paper may be thrown into the water in order to prevent it from bumping during the boiling.

FIG. 28.

MULTIPLE WATER-BATH.

When the evaporating dish is placed on the top of the beaker the escape of the steam may possibly be prevented. If this should be the case, some strips of paper may be inserted between the bottom of the dish and the edge of the beaker.

In a large laboratory used by many students the steam-baths are often provided by openings closed with lids (Fig. 45) upon the top of a range of steam-ovens in the combined arrangement shown in Fig. 75 (1377).

39. Concentration and Crystallisation. Sometimes only a part of the liquid is evaporated for the purpose of "concentrating" the solution.

When a hot solution has been sufficiently concentrated, it will frequently deposit "crystals" of the dissolved substance as it cools.

FIG. 29.

SIMPLE WATER-BATH.

Soluble substances are often dissolved, and then crystallised from their solution in this way, in order to free them from impurities.

EXPERIMENT 8.—Concentrate the copper sulphate solution which was prepared in Exp. 4 (page 19), and allow the liquid to cool. If sufficient water has been evaporated, crystals will form.

In order to ascertain whether the hot solution will crystallise on cooling, pour about two cubic centimetres (cc.) of the solution into a test-tube and cool the test-tube in water; if crystals form, the rest of the solution may be allowed to cool in the air.

Keep the copper sulphate solution in the dish for future use.

PRECIPITATION.

40. Precipitation by a Liquid.—When two clear and transparent solutions are mixed together, they frequently become more or less turbid or opaque, owing to particles of a solid substance being formed in the liquid. A solid substance thus produced is called a "precipitate," and the process of producing a precipitate is termed "precipitation."

A substance is frequently removed from solution by causing it to form an insoluble compound or precipitate. The substances which are added for this purpose are termed "reagents" or "precipitants": they are commonly liquids.

In producing a precipitate, care must be taken that the two solutions are well mixed. Mixture may be effected by warming the bottom of the test-tube in the flame, by stirring the liquid with a glass rod, or by pouring the liquid from one vessel to another.

A precipitate often appears more rapidly when the liquid is vigorously shaken, or when it is warmed.

EXPERIMENT 9.—Pour some barium chloride solution into a test-tube, and add ammonium carbonate solution. A white precipitate of barium carbonate will form. Keep the precipitate and liquid in the test-tube for future use.

In this instance barium chloride and ammonium carbonate may be readily dissolved in separate portions of water. But if these solutions are mixed, two different substances, ammonium chloride and barium carbonate, are produced. The former of these remains dissolved in the water ; but the latter is insoluble, and therefore separates as a fine powder in the liquid.

Precipitates differ much in colour and in general appearance and properties ; they are therefore frequently produced, by the addition of suitable reagents, in order to show the presence of a substance. Precipitates are also produced for the purpose of separating one substance from another.

The appearance of a precipitate is usually described by its colour and by its condition. It is "flocculent," if it forms in flock-like masses ; "crystalline," if it consists of small particles which are seen to be crystals under a lens or microscope ; "gelatinous," if it is jelly-like in its consistency. The formation of a slight precipitate may cause only a "turbidity" in a liquid.

The day-light colour of a precipitate is always given in the following text, and this may be changed when the precipitate is seen in some kinds of artificial light. The true colour, however, is seen at night if the precipitate is illuminated by the electric arc, or by a piece of burning magnesium ribbon.

41. **Precipitation by a Solid Reagent** is occasionally resorted to. Thus a metal is not unfrequently precipitated from the solution of its salt by the immersion in it of another metal.

EXPERIMENT 10.—Dip a clean penknife-blade into some of the copper sulphate solution (Exp. 8), to which a few drops of sulphuric acid have been added. After a short time metallic copper will be precipitated from the solution and will cover the iron as a red film.

DECANTATION AND FILTRATION.

The Processes of Decantation and Filtration serve to separate a precipitate from a liquid in which it is suspended. Decantation is sometimes preferred because with suitable precipitates it is more rapidly and simply carried out than filtration, and it leaves the precipitate in the vessel ready for immediate further treatment.

42. **The Process of Decantation** serves to separate a heavy precipitate, which settles rapidly, from the liquid out of which it has subsided.

For this purpose, the vessel containing the liquid and precipitate is allowed to stand until the precipitate has settled. The liquid

is then carefully poured off, or "decanted," by gently inclining the vessel. A wetted glass rod, pressed against the edge or lip of the vessel (Fig. 30), helps to prevent the precipitate from being disturbed while the liquid is flowing away from it.

If the process of decantation is carefully performed, it will separate the liquid almost completely and in a clear condition.

EXPERIMENT 11.—Add boiling dilute sulphuric acid to some boiling solution of barium chloride. A heavy precipitate of barium sulphate will be formed. This precipitate may be readily separated from the liquid by decantation. Keep the precipitate in the test-tube for future use.

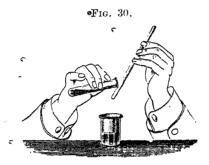



FIG. 30.

DECANTATION OF A LIQUID.

43. **Filtration.**—The liquid containing the precipitate is poured into a cone of porous paper. The liquid itself runs through the pores of the paper, but the solid particles of the precipitate are retained upon the surface of the paper.

The paper employed is called "filter-paper," and the liquid which has passed through the filter is termed the "filtrate."

A filtrate may frequently be coloured by some substance dissolved in it, but it should be perfectly free from turbidity caused by solid particles suspended in it.

The ordinary process of filtration employed in chemical analysis is described below, methods of filtration on a larger scale are described in paragraphs 1391, 1392.

Prepare a filter for filtration as is directed below.

EXPERIMENT 12.—Measure a glass funnel (Fig. 48) along its sloping side from shoulder to rim. Select a circular filter paper, the radius of which is somewhat less than this in length: fold it across into a semicircle, then fold it again at right angles into a quarter of a circle; now open out either of the sides, so as to form a little conical bag (*d*, Fig. 32). This forms an ordinary filter.

FIG. 31.

FUNNEL.

Filters $3\frac{1}{2}$ and $4\frac{1}{2}$ inches (9 and 11 cm.) in diameter are convenient for ordinary purposes.

If ready-cut filters of suitable size are not at hand, cut from a sheet of filter-paper a square piece, the edge of which is rather less than double the

length of the side of the funnel. Fold it over along the line (*a*, Fig. 32, then again along the dotted line (*b*). This gives a square (*c*) which at one angle has four free corners; these are removed by cutting with a pair of scissors along the curved dotted lines shown in (*c*).

The filter is now made and only requires to be opened. By separating the curved edges so that they form a circle, three remaining on one side of the circle and one on the other, a little closed pointed paper bag is formed (*d*).

A filter of the same shape, but of uniform thickness, may be made from half an ordinary circular filter-paper, or from half of the circular flat paper formed by opening out the filter (*d*). This semicircular paper is folded into a quadrant shape, and the two radial edges are doubled over together several times, the fold being pressed down with the finger nail. The unused half of the filter (Fig. 32, *d*) is absent in the filter which is formed by opening this paper, and filtration is more rapid in consequence.

The folded filter is now gently pressed with dry fingers into the dry funnel, and the folding is altered if necessary until the paper fits the glass closely. It is then moistened all over with distilled water from the wash-bottle and is ready for use.

FIG. 32.

FOLDING AND CUTTING FILTER.

This preliminary moistening of the filter-paper must not be neglected, since if the liquid which contains the precipitate is poured upon a dry filter, some particles of the precipitate may lodge between the fibres of the paper; the paper then shrinks on being wetted inclosing the solid particles, and these choke the pores of the filter and seriously retard the filtration.

During the filtration of a liquid the funnel may be placed with its neck in a test-tube, which is supported in the test-tube stand. Care must, however, be taken that the inside of the upper part of the test-tube is dry, and that there is a space between the neck of the funnel and the inside of the tube; since, if the egress of air from the test-tube is prevented, the filtration will be stopped. The funnel is therefore preferably supported upon the ring of a wooden filter-stand (Fig. 33, page 28); and the filtrate is received in a small beaker standing beneath the funnel, instead of in a test-tube.

As has been already stated, the upper edge of the filter must always be below the rim of the funnel; and when the liquid, which is to be filtered, is being poured into the filter, care must be taken not to let it reach the upper edge of the filter-paper.

The precipitate should not more than half fill the filter, else it cannot conveniently be washed.

EXPERIMENT 13.—Pour the liquid containing the precipitate of barium carbonate, from Exp. 9 (page 24), through the filter. If the above directions have been carried out, and no hole has been made in the paper, while it is being prepared or fitted into the funnel, the filtrate will run through perfectly clear, leaving the barium carbonate on the filter. Keep the filter and precipitate in the funnel for future use.

FIG. 33.

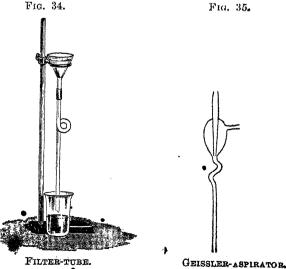
FILTER-STAND.

Sometimes the filtrate passes away from the filter in a turbid condition. In order to remove this turbidity, the turbid portion of the filtrate must be poured once or twice through the same filter. Or the turbidity may be prevented by pouring the liquid at once through a double filter, which is prepared by folding two filter-papers together as one: a double filtration is thus secured in one operation.

It should be borne in mind that a hot liquid passes through the filter more quickly than a cold one. Hence, if it is not inadmissible for other reasons, a solution should always be heated before it is filtered.

44. Accelerated Filtration.—Methods for expediting the filtration of arge quantities of solids from liquids are described in pars. 1391, 1392. But

FIG. 34. FIG. 35.

FILTER-TUBE. GEISSLER-ASPIRATOR.

it is often desirable to hasten the process of filtration of a liquid in an ordinary funnel, more especially when a flocculent precipitate is being separated from the liquid. This may be effected either by attaching a suitable tube to the funnel (1), or by means of a filter-pump or an aspirator (2).

(1) One of the simplest means of increasing the rate of filtration is to attach to the funnel a glass tube, about 2 feet (60 cm.) long, bent as is shown in Fig. 34. As soon as the filtrate has filled this tube, the weight of the column of liquid tends to draw the liquid through the filter, and the rate of filtration is accordingly increased.

Another simple method is to attach to the funnel a straight piece of glass about 2 feet (60 cm.) in length and 1 millimetre in bore. The weight of the liquid column which is suspended in this tube pulls the liquid through the filter.

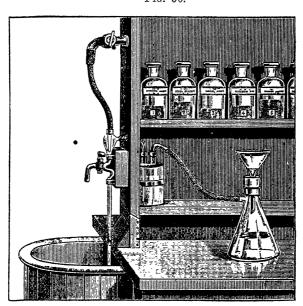



FIG. 36.

WATER FILTER-PUMP, OR ASPIRATOR.

(2) A Filter-pump, or Aspirator, which applies suction to the neck of the funnel, is frequently used to hasten filtration.

The accompanying illustration (Fig. 36) shows a convenient arrangement for this purpose. The glass Geissler-aspirator (Fig. 35) is shown over the sink, connected by stout rubber tubing with the high pressure water-tap. When the water is turned on and flows through the aspirator, air is sucked from the thick-glass conical tubulated filter-flask; and the atmospheric pressure, acting on the liquid in the funnel, is thus utilised for forcing the liquid through the filter.

The two-necked Woulffe's bottle is interposed between the aspirator and the filter-flask in order to prevent the water in the aspirator from entering the flask.

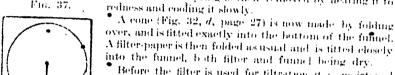
The neck of the funnel is fitted by a rubber cork into the neck of the conical filter-flask; and in order that the pressure which is exerted on the point

of the filter-paper may not burst it, either toughened filter paper may be used, or the ordinary filter-paper may be supported beneath by a small cone of parchment-paper or of platinum.

The cone is cut from a piece of platinum foil or parchment paper measuring about $1\frac{1}{2}$ × $1\frac{1}{2}$ inch (Fig. 37). A hole is pierced by a pin near the middle, a cut is made from the edge to this hole, and the corners are removed by cutting round in a circle which has the pin hole for its centre. If the metal foil is used, the spring is then removed by heating it to redness and cooling it slowly.

FIG. 37.

PLATINUM FILTER-CONE.

A cone (Fig. 32, *d*, page 27) is now made by folding over, and is fitted exactly into the bottom of the funnel. A filter-paper is then folded as usual and is fitted closely into the funnel, both filter and funnel being dry.

Before the filter is used for filtration it is moistened with water, and is then gently pressed, where necessary, with the fingers until it adheres to the funnel; the upper edge of the filter especially requires to be carefully pressed against the glass in this way. The filter is now tested, by filling it with distilled water and setting the pump in action.

If the paper fits properly and has been pressed into contact with the funnel, no air-bubbles will be sucked down the neck of the funnel until the whole of the water has passed through the filter. Any air leakage must be stopped by pressing the paper against the funnel where such leakage occurs.

Besides expediting the filtration and washing of precipitates, such an arrangement also enables the precipitate to be dried to a great extent by sucking air through it after the liquid has passed away.

The aspirator may be replaced by other forms of apparatus for producing suction. A common hand-syringe may be used, but this is liable to be attacked by acid vapours if it is made of brass.

A Special form of Receiver is represented in Fig. 38 to serve as a substitute for the conical flask. It consists of an ordinary separating funnel, *F*, which is closed with a doubly perforated rubber cork.

One perforation carries the funnel, which is used for filtration. Into the other is inserted a branched tube, one limb of which (*b*) is connected with the filter-pump, while the other (*a*) can be opened to the atmosphere by turning the stopcock.

FIG. 38.

SPECIAL RECEIVER FOR THE FILTRATE.

The use of this receiver renders it possible to withdraw a portion of the filtrate during the process of filtration, by opening simultaneously the stopcocks *a*, *c* and stopping the action of the filter-pump.

WASHING THE PRECIPITATE.

45. The Washing of a Precipitate, after it has been separated from the liquid in which it was suspended, is usually necessary in order to free the precipitate from the adhering solution.

If the precipitate has been filtered, it is washed upon the filter (46); if it has been separated by decantation, it is usually washed by decantation (47).

46. Washing the Precipitate on the Filter.—The following directions will serve to explain how this process is carried out, and will indicate what precautions should be observed in order to secure success. The washing process may be hastened by employing the devices which have been already described in par. 44.

EXPERIMENT 14.—Support the funnel, which contains the filter and the barium carbonate precipitate from Exp. 13 (page 28), in a filter-stand above a beaker or flask (Fig. 33, page 28). Blow into the filter a fine stream of hot distilled water from the wash-bottle (17), so directing the jet as to stir up the precipitate. Fill the paper in this way with water to within a short distance from its edge, and let the water run through perfectly, and repeat these processes three or four times, letting the water run through completely each time before adding a fresh quantity.

The precipitate and the filter should now be free from everything soluble in water, and the water which passes through the filter will therefore be tasteless.

Ascertain whether the washing is complete, by collecting the last few drops of the washing-water in a clean test-tube, and testing whether it contains any chloride by adding to the liquid a drop of silver nitrate solution; no turbidity must be produced. If turbidity appears, the washing must be continued and the washing-water must be tested again.

The process of washing must be continued, until silver nitrate produces no turbidity when it is added to the last portions of the water running from the funnel.

Reserve this precipitate in the filter for further use.

47. Washing the Precipitate by Decantation.—This method may be adopted with a suitable precipitate, and may often usefully precede the separation of the precipitate from the liquid by filtration, the earlier stages of washing being carried out by decantation.

EXPERIMENT 15.—The precipitate of barium sulphate from Exp. 11 (page 26) may be washed by decantation as follows.

Hot water is poured into the vessel containing the precipitate, and the water is shaken, stirred, or boiled with the precipitate, which is then allowed to settle. As soon as the water has become clear, it is poured off as completely as possible in the way shown in Fig. 30 (page 26).

By repeating this washing process several times, with the addition of fresh portions of boiling distilled water, the precipitate may be entirely freed from the adhering solution.

While the washing-water is being poured off it should be occasionally tested with blue litmus-paper, in order to ascertain when it ceases to redden the paper and is therefore free from acid. As soon as the washing-water is quite free from acid, the precipitate may be considered to be thoroughly washed.

Reserve this precipitate for further use (56), after filtering it off on a small filter, and putting it aside to dry.

It is usual to Ascertain when the Washing of a Precipitate is Complete, by testing the washing-water for some soluble substance which is being removed by the washing. That substance is usually tested for which is most readily detected. Experiments 14 and 15 serve to illustrate this statement.

DRYING THE PRECIPITATE.

48. **A Precipitate may be dried** by supporting the funnel on a hollow tin cone or cylinder, called a "filter-dryer" (Fig. 39) which is placed on a piece of iron wire gauze on a tripod-stand, and heated over the flame of a rose-burner turned very low; or the filter dryer may be placed upon a heated iron plate or sand-bath.

FIG. 39.

FILTER-DRYER.

The filter may be dried more quickly by allowing it to drain for a time, and then opening it out and spreading it upon a piece of wire-gauze supported upon a tripod-stand or upon the ring of a retort stand, a small flame from the rose-burner being placed at some distance beneath it. The handling of the moist filter is facilitated if it has first been laid upon a pile of several filters, which will absorb the water.

The filter is by these means exposed to a current of hot air, which rapidly dries the precipitate. Care must be taken to regulate the heat so as not to char the filter.

The Steam-oven may be used to secure a more gradual but safer process of drying. The funnel is placed in the steam-oven as is shown in Fig. 40, but the conical support is usually unnecessary, since most ovens have perforated shelves and the funnel is supported by passing its stem through one of these perforations.

A combined system of steam-ovens and water-still is shown in Fig. 75 (1377) for use in a large laboratory, and in some laboratories the steam-ovens are heated by steam supplied from a large general boiler. These steam-ovens will be available for drying precipitates.

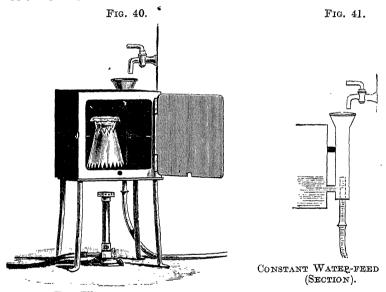
But if this general system is not available the separate steam-oven shown

in Fig. 40 may be used. In this oven water is boiled in the space between the double-cased copper oven, the escaping steam being condensed and returned to the water-jacket by connecting the steam-outlet with a long piece of "composition" tubing fixed on the laboratory wall, and thus maintaining the water level. This tube must be sufficiently long to condense all the steam generated when the water is gently and steadily boiling.

Another method of maintaining the water-level is shown in section in Fig. 41, where a slow drip from the water-supply pipes falls into a funnel feed-tube at the side of the oven, any excess of water escaping by a central out-flow pipe into the waste.

It is well to avoid a constant feed of *hard* water to the steam-oven, since the incrustation which gradually forms in the water-space is removed with difficulty. Accordingly if the oven is not heated by steam, or the interspace constantly fed, as directed above, by the return of the condensed steam, a raised vessel containing soft or distilled water may be used to feed the supply tap (Fig. 41).

FIG. 40. THE WATER-OVEN.

FIG. 41. CONSTANT WATER-FEED (SECTION).

The air-inlet pipe to the bottom of the oven passes through the hot water and delivers hot air in the interior, an outlet for air being provided at the top of the oven. It is convenient to have a piece of glass let into a metal frame for the door, so as to render the interior visible without opening the door.

The Air-oven (Fig. 42, p. 34) may be employed instead of the steam-oven. It is similar in construction, but is heated directly by a gas-flame placed beneath it, the temperature of the interior being suitably adjusted by regulating the flame.

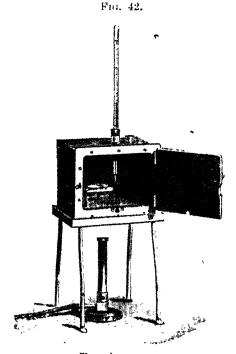
The requisite temperature may be maintained by occasional observation of the thermometer, or a special thermal gas regulator may be enclosed in the interior of the oven, and will serve to automatically control the gas-supply.

The air-oven can be used when drying temperatures above 100° C. are required; but it must be remembered that the metal sides of the bath are much hotter than the internal air, and that the drying substance should therefore be supported out of contact with the oven, as is shown in the figure, if it is to be heated only to the temperature registered by the thermometer.

The air-oven may be heated electrically instead of using a gas-burner, and with suitable resistances a considerable range of temperature is thus obtainable.

REMOVING THE PRECIPITATE FROM THE FILTER.

49. Removal of Part of the Precipitate from the Filter.—A small portion of a moist precipitate may be taken from the filter by dipping the end of a glass rod into it. If a watch-glass, or the

FIG. 42.

THE AIR-OVEN.

interior of a test-tube, is then touched with the end of the rod, the precipitate is deposited upon the surface of the glass, and may be subjected to further test or examination.

A larger quantity of the precipitate may be taken out of the filter by means of a glass spatula, made by flattening out the end of a glass rod which has been softened in the flame.

50. Removal of the Whole of the Precipitate from the Filter.—If the precipitate is to be removed from the filter as com-

pletely as possible, several methods are available. One or other of those described below under **a**, **b**, **c**, **d**, **e**, and **f**, must be chosen according to circumstances. Of these the methods described under **a**, **e** and **f** are in most common use.

(a.) **Washing down the Precipitate through the neck of the Funnel.**—A hole may be made in the bottom of the filter by means of a thin glass rod (15), which is pushed down through the neck of the funnel. The precipitate is then easily washed down into a vessel, placed beneath the funnel, by a fine stream of liquid from the wash-bottle.

(b.) **Washing out the Precipitate from the Rim of the Funnel.**—The funnel may be held with its neck horizontal, and with its rim just inside the edge of a porcelain dish (Fig. 43). The precipitate is then washed out of the filter by directing a fine stream of water from a wash-bottle against the inside.

Fig. 43.

Washing the Precipitate out of the Filter.

(c.) **Removal of the Filter with the Precipitate from the Funnel, followed by rinsing off the Precipitate.**—The filter with the precipitate is allowed to remain in the funnel for some time, in order to permit as much water as possible to drain away. The filter is then carefully taken out of the funnel and is further dried, if necessary, by laying it upon several folds of filter-paper. After the portions which contain no precipitate have been removed, the filter is spread out inside a porcelain dish.

The liquid, with which the precipitate is to be treated, is then poured into the dish; and this liquid is shaken round in the dish, and the filter is carefully rubbed with the rounded end of a glass rod, until the precipitate has been removed from the paper. With a little care this may be effected without tearing the paper. The filter-paper is then removed from the liquid by means of the glass rod.

(d.) **Removal of the Filter with the Precipitate, followed by Scraping off the Precipitate.**—If it is undesirable to add a liquid to the precipitate upon the filter, the precipitate is allowed to drain for a short time; it is then further drained, if necessary, by removing the filter from the funnel and laying it upon several filter-papers.

The filter is then spread out upon a flat piece of glass, and the precipitate is carefully scraped off with a glass rod which is pressed flat upon the paper, or with a small glass spatula (49).

This method is usually the most imperfect, but is frequently the best for other reasons.

(e.) **Removal of the Precipitate by Dissolving it in the Filter.**—If a precipitate is to be dissolved off the filter, the liquid, which is to be used as a solvent, is heated and is then poured upon the precipitate. The solvent will run through the filter into a vessel placed below the funnel, and will take with it the precipitate in solution.

After the liquid has passed through the filter, it should be heated again and once more poured upon the precipitate, if the latter is not entirely dissolved. The liquid is reheated and returned to the filter in this way as long as anything remains undissolved. If any portion of the precipitate still remains, it must be removed by using a fresh portion of the solvent.

EXPERIMENT 16.—Remove in this way the precipitate of barium carbonate (Exp. 14, page 31) from the filter, by means of hot dilute hydrochloric acid.

(f.) **Removal of the Precipitate by Rinsing it through the Filter with the Solvent.**—A precipitate may also be removed from the filter by means of the liquid with which it is to be treated or dissolved, in the following manner.

The funnel is supported over a suitable vessel. The liquid is poured in and is quickly stirred up with the precipitate by means of a thin glass rod. The bottom of the filter is then pushed out through the neck of the funnel by the glass rod. The liquid will now flow through the neck of the funnel, carrying the precipitate with it.

If some of the precipitate remains on the filter, the liquid must be poured again through the funnel, and by repeating this process all the precipitate may be removed.

USE OF TEST-PAPERS.

51. **Litmus and Turmeric Test-papers.**—The two vegetable colouring substances litmus and turmeric undergo marked changes of colour when they are acted upon by certain substances. These changes serve to indicate whether a liquid or gas is "acid," or "alkaline": if no change occurs, it may be inferred to be "neutral."

The analyst is usually provided with slips of paper which have been stained with solutions of these colouring substances. These slips of paper are known as "test-papers." The different papers are easily distinguished by their colours. The following experiments will explain their use.

52. **Acid, Alkaline, or Neutral Reaction** in a liquid is ascertained by the behaviour of the liquid with these test-papers.

EXPERIMENT 17.—Dip a clean dry glass rod successively into dilute hydrochloric acid, into ammonium hydroxide solution, and into barium chloride solution. After each immersion of the rod, draw its end, wetted with the solution, successively across blue litmus-paper, red litmus-paper, and yellow turmeric-paper. The following results will be obtained.

Hydrochloric acid will redden blue litmus, but will not alter the colour of red litmus or of turmeric; it possesses an "acid reaction."

Ammonium hydroxide solution will not affect the colour of blue litmus, but will turn red litmus blue and turmeric brown; it shows "alkaline reaction."

Barium chloride solution will not affect the colour of any one of the test-papers: it is "neutral."

Each of these liquids is typical of a large class of substances, in so far as its behaviour with these test-papers is concerned.

53. **Neutralisation: Addition of Acid or of Alkali in Excess.**—It is occasionally necessary to exactly neutralise an acid liquid by means of an alkaline liquid or vice versâ. The acid or alkali must also often be added in excess. The following experiment explains how these processes are effected.

EXPERIMENT 18.—Pour some dilute hydrochloric acid into a porcelain dish. Add solution of ammonium hydroxide drop by drop, constantly stirring the liquid with a glass rod and touching the wet end of the rod against a piece of blue litmus-paper.

By proceeding cautiously, a point may be reached at which the liquid does not affect the colour of either blue or red litmus-paper; the acid is then said to have been "neutralised" by the alkaline liquid.

The latter part of the process of neutralising the acid liquid should be completed by the addition of the alkaline solution in a very dilute condition, since the addition of an excess of the alkaline solution is thus more readily avoided.

Add another drop of ammonium hydroxide: the liquid will now have acquired an alkaline reaction: the alkaline solution is accordingly said to have been added "in excess."

By a similar procedure an alkaline solution may be neutralised with an acid, and may then be mixed with acid in excess or acidified.

54. **General Remarks on Test-papers.**—In choosing between red litmus and turmeric test-papers for the detection of alkaline reaction, it should be remembered that turmeric-paper is usually

more sensitive than red litmus-paper, since red litmus-paper may contain an excess of acid.

A turbid liquid will often form a deposit when it is placed upon the test-paper, and this may conceal the colour of the paper. The colour will, however, usually be visible on the back of the paper if it is unglazed. If the paper is glazed, the colour will be seen after the deposit has been washed off by a stream of distilled water from the wash-bottle.

Test-papers must always be kept in a stoppered bottle, in order to guard them against undergoing change by the action of gases contained in the laboratory air. The bottle should be shielded from light as much as possible, since these vegetable colours fade under the action of sunlight or strong daylight: this is especially the case with turmeric paper.

SIMPLE IGNITION.

55. **Solid Substances are Heated strongly, or Ignited,** in order to study the effect of heat upon them, since by this means their composition or nature is frequently revealed more or less completely. Ignition also serves to remove volatile from non-volatile substances.

It is a necessary condition of the process of "simple ignition" that the substance, which is being heated, shall not suffer change by contact either with the flame, or with the substance of the vessel or support, or by admixture with chemical reagents. It is usually, however, subjected to change by contact with the oxygen of the air.

EXPERIMENT 19.—Heat some white **zinc oxide** in a small ignition-tube (13). The hot substance will be *lemon-yellow*, but the colour will change to *white* again as the oxide cools. These changes of colour are characteristic of zinc oxide.

In the early stage of the heating, drops of water will probably condense in the upper part of the tube: this shows that adherent moisture was present with the oxide. Ignition in a tube is often employed to detect the presence of water in a substance.

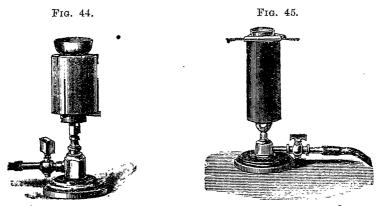
EXPERIMENT 20.—Heat a little **mercuric oxide** in a small test-tube or ignition-tube. After a short time minute shining drops of the metal mercury will be seen in the upper part of the tube. If a splinter of wood with a spark at its end is now held in the tube, it will burst into flame. The behaviour of this red powder when it is ignited, shows that it contains the elements mercury and oxygen.

EXPERIMENT 21.—Heat a few particles of **charcoal powder** on platinum foil, by directing the tip of the blowpipe-flame against the under surface of the foil. The charcoal will be slowly burnt away by the oxygen of the air, showing that the black substance consists of carbon.

EXPERIMENT 22.—Heat a small piece of **ammonium chloride** in an ignition-tube. The ammonium chloride will pass off as vapour or "volatilise," and the vapour will cool in the upper part of the tube forming a coating or "sublimate." This proves that the salt is volatile.

EXPERIMENT 23.—Heat in the same way a small piece of **potassium chloride.** This will melt or "fuse," but will not pass off as vapour. It will become solid again on cooling. Potassium chloride is almost non-volatile at the flame temperature.

Hence if a mixture of ammonium chloride and potassium chloride is heated on platinum foil, the potassium chloride alone will be

FIG. 44. FIG. 45.

IGNITION OVER THE ARGAND-BURNER.

left in the residue, since the ammonium chloride will be removed as vapour.

If the quantity of the substance to be ignited is large, it is usually heated in a porcelain or platinum vessel over the Bunsen-, Teclu-, or blowpipe-flame (Fig. 64, 1308).

Small quantities of substance may be conveniently ignited in little porcelain or platinum capsules over an Argand burner from which the gauze top has been removed (Figs. 44, 45).

The luminous flame must not be allowed to touch the capsule, since it soils the surface and also damages platinum.

TREATMENT WITH FUSED REAGENTS.

56. A Substance is often Heated with certain Solid Reagents until they fuse or melt, in order to cause chemical changes to occur between the substance and the reagents.

EXPERIMENT 24.—Mix a little of the dry **barium sulphate** (Exp. 15, page 31), which is insoluble in water and in acids, with a mixture of sodium and potassium carbonates, and heat the mixture on platinum foil (see *Note* below) until the alkaline carbonates fuse. Maintain the salts in a fused condition for several minutes. The following change will then have taken place :—

$$BaSO_4 + Na_2CO_3 = BaCO_3 + Na_2SO_4.$$

Now treat the cool product with water. The sodium sulphate will be dissolved. Separate the residual barium carbonate by filtration, and wash it. Then treat it with dilute HCl : the insoluble carbonate will dissolve as chloride : $BaCO_3 + 2HCl = BaCl_2 + H_2O + CO_2$. The original barium sulphate is thus converted into chloride which is obtained in solution.

A substance which cannot be dissolved in water or in acids may frequently be converted into a soluble substance in a similar way to that just described.

The mixture of alkaline carbonates, which is used for the purpose, is generally known as "fusion mixture."

Note.—In this experiment, and in other experiments for which platinum foil is used, the platinum may be replaced by a small porcelain crucible or by a fragment from a broken porcelain dish. If porcelain, however, replaces platinum, a somewhat more powerful burner is necessary to produce the fusion.

Sometimes the treatment with fused reagents yields a characteristic result, which serves to detect the presence of a substance.

EXPERIMENT 25.—Place a little powdered **sodium carbonate and potassium nitrate** on a piece of platinum-foil (see *Note* above), and then add a minute quantity of **manganese dioxide.** Hold the foil with crucible-tongs in the top of the Bunsen-flame, or heat the under surface of the foil with the point of the blowpipe-flame. The mass will soon melt or fuse. Keep the substances in a melted state for a short time, and then allow the mixture to cool.

A *bluish-green* mass will remain upon the foil, the colour of which is due to the sodium manganate which has been formed by the fusion. This colour is produced only when manganese is present, and the above process therefore serves as a test for that metal.

In the above experiments (19 to 25) the gases of the flame are

not allowed to take any part in the change which is described. In the following cases the flame-gases aid in producing the reaction.

FLAME REACTIONS WITH REAGENTS.

57. **The Gases of the Blowpipe-flame** (11) **or of the Bunsen-flame may play the part of Reagents** in affecting the composition of the substance which is being heated. In order to understand the nature of these changes the structure of the flame must be carefully observed.

In a well-formed blowpipe-flame or Bunsen-flame two parts may be distinguished: the "inner-flame," which is blue and pointed; and around and beyond this an almost colourless flame, which is commonly known as the "outer-flame."

For ordinary mouth-blowpipe operations a luminous gas flame should be used, and the size of the flame should be so adjusted that both the inner and outer blowpipe flames are sharply defined; or the Bunsen-flame may be used after closing the air-holes more or less completely.

The Inner-flame is often called the "reducing or deoxidising flame," because it separates or reduces metals from their oxides and from many of their compounds, and in general deoxidises substances. This deoxidising power is due to the action of the hot but incompletely burnt combustible matter, which is present in this part of the flame.

The inner flame is obtained of large size by placing the tip of the blowpipe nozzle only in the outer edge of the flame.

The Outer-flame is also known as the "oxidising-flame," because it changes metals into their oxides, and oxidises many other substances, by supplying them with oxygen at a high temperature.

The size of the outer-flame is increased by pushing the nozzle of the blowpipe into the interior of the Bunsen-flame.

In the following processes the results obtained will usually vary when the substance is heated in the inner-flame or in the outer-flame.

58. **The Borax-bead—Fusion with Borax.**—When certain metals and their compounds are fused with borax, they are converted into coloured borates. The colour of each of these borates is characteristic, either in itself or in the changes which it undergoes in the outer and inner flames.

The method of making the borax-bead is explained in Exp. 26. Its use for testing is illustrated by Exp. 27.

EXPERIMENT 26.—Place a little powdered borax on a watch-glass. Moisten the loop of a piece of mounted platinum-wire (14), and dip it into the borax. Then hold the loop with the adhering powder in the outer blowpipe-flame until the borax melts.

If the bead thus formed does not fill the loop, dip the melted bead again into the borax; more powder will adhere and may be melted in the flame. In this way powder is to be constantly added, until a drop or bead is obtained which completely fills the loop. This bead must be perfectly colourless and transparent when it is cold.

If the melted bead easily drops from the wire, either the loop or the bead is too large. A loop which is somewhat less than an eighth of an inch (3 mm.) across answers well; it may be made by rolling the tip of the wire round a piece of stout wire. If the bead is too large, remove a portion of it by giving the wire a slight jerk while the borax is in a fused condition.

If the bead thus formed shows any colour, it is jerked off while it is in a fused condition, and another bead is made from fresh borax. This process is repeated, if necessary, until a bead is obtained, which is colourless after it has been heated in the outer blowpipe-flame.

EXPERIMENT 27.—Moisten the clear cold borax-bead, and dip it into some finely-powdered manganese dioxide; a few minute particles only are to be thus attached to the bead. Then fuse this substance into the bead, by heating it for a short time in the tip of the *outer* blowpipe-flame.

Examine the colour of the bead at once by looking through it at a piece of white paper, or at a window-light or bright flame. It will be *purple* or *amethyst-red* while hot, and the colour will not alter when the bead has cooled.

Now heat the bead again for some time in the tip of the *inner* blowpipe-flame. Its colour will vanish. The colour will, however, reappear when the bead is heated at the tip of the outer blowpipe flame.

These changes of colour in the borax bead are characteristic of the metal manganese and its compounds.

General Remarks on the Borax-bead.—A beginner often obtains an opaque bead in the above experiment, because too much manganese oxide has been used. The bead should then be fused again, and a portion of it should be shaken off and replaced by fresh borax.

When the test with the borax-bead is finished, the bead is detached, while it is still fused, by giving the wire a sudden jerk; or the bead may be removed, after it has cooled, by crushing it on a hard flat surface by a blow with the pestle.

Two mounted platinum-wires should be kept, and their loops should always be immersed in dilute hydrochloric acid when the wires are not in use. They

will then only require to be washed with water before they are employed for the above test.

59. **The Microcosmic-bead.**—Some substances give more decisive colorations to a fused bead of microcosmic salt ($NaNH_4HPO_4.4H_2O$) in the platinum-wire loop, than to a bead of borax prepared as has been described in the preceding paragraph. The platinum-wire loop for this test must be made smaller than for borax, else the bead easily drops out of the loop.

60. **Ignition on Charcoal in the Blowpipe-flame.**—Wood charcoal is often employed as a support for substances which are to be strongly heated in the blowpipe-flame. It possesses the advantage of being cheap and infusible, and a bad conductor of heat.

Charcoal is, however, often used on account of the reducing or deoxidising power which it can exert at a high temperature. This renders it entirely unsuitable for oxidising processes such as that described in Exp. 25 (56).

Ignition on charcoal, therefore, serves chiefly to detect the presence of the heavier metals in their compounds. These are smelted out by the reducing action of the inner blowpipe-flame, aided by that of the red-hot charcoal. The assistance of fused reagents is, however, often necessary or at least advantageous.

The vapours of some metals, which have been thus smelted out, burn as they leave the charcoal, and the metallic oxides thus formed are deposited as "incrustations." The white ash, which is left by combustion of the charcoal, must not be mistaken for such an incrustation.

EXPERIMENT 28.—Choose a piece of wood charcoal which is free from large cracks, and which does not crackle or spit when it is heated in the blowpipe-flame; or, better still use a specially prepared hard charcoal block, which may be purchased and is more suitable and durable. Scoop out a *small* hollow near one end of it, with a knife or with a charcoal-borer.

Place in this cavity a small quantity of a mixture of powdered lead acetate and sodium carbonate. Then heat this mixture in the inner blowpipe-flame, holding the charcoal in such a way that the flame plays over its surface (Fig. 46, page 44).

Bright globules of lead will soon be visible in the cavity; and when the charcoal is removed from the flame, the surrounding surface will be found to be coloured with a *yellow incrustation.*

Take one of the little globules of metal from the charcoal with the point of a penknife, and strike it smartly with the pestle on the bottom of the inverted mortar. It will flatten out into a cake, showing that the metal is *malleable* and not *brittle.*

Detach another metallic globule, cleanse it from charcoal by rolling it between the moistened finger-tips, transfix it on the

point of the penknife blade, and rub it on some paper. It will be found to mark the paper as a black-lead pencil does.

Lead compounds are characterised by giving a yellow incrustation, and malleable globules which are soft enough to mark paper

FIG. 46.

IGNITION ON CHARCOAL.

when they are subjected to this test on charcoal. This reaction therefore serves to detect the presence of lead in its compounds.

61. Washing and Levigation of the Residue left on the Charcoal.—The metallic globules, which have been obtained in the preceding experiment, are usually visible, even without the aid of a lens. They are also usually detachable from the charcoal, and do not require the following treatment.

FIG. 47.

WASHING BY LEVIGATION.

But fine metallic particles or scales can often only be separated and detected after the fused residue has cooled and been detached from the charcoal with the point of a penknife, and has then been washed by levigation.

With this object, the detached residue is crushed in a mortar, or in a porcelain dish, with a little water. The water is then quickly decanted down the wet pestle, which is pressed against the edge of the vessel (Fig. 47). The light suspended particles of charcoal, together with soluble substances, are thus poured off; while the heavier and insoluble metallic particles are left in the vessel. By repeating this process of "levigation," the metal may be obtained free from soluble substances and from charcoal; it may then be further examined by a lens, or may be tested with a magnet or by other means.

It may be noted that the addition of a little potassium cyanide to the mixture, before it is heated on the charcoal, will usually much facilitate the process of smelting out the metal, and will assist in bringing it into the globular condition.

EXPERIMENT 29.—Fuse some sodium carbonate with a little copper sulphate on charcoal in the inner blowpipe-flame, and levigate the residue as is directed above. Little *red scales* of copper will be obtained.

EXPERIMENT 30.—Treat in the same way a mixture of ferrous sulphate and sodium carbonate: *a grey powder*, consisting of metallic iron, will remain. When this powder is touched under water with the point of a magnetised penknife, it will attach itself in the form of a tuft.

FLAME-COLORATIONS.

62. **Characteristic Colours are imparted to a Non-luminous Flame** by the vapours which many substances emit at a high temperature.

The blowpipe-flame may be employed to obtain these colorations. A Bunsen-flame also answers the purpose well, but on account of the lower temperature of this flame, many colorations are not obtained with promptness or intensity.

FIG. 48.

BUNSEN-BURNER WITH CHIMNEY.

When the Bunsen-flame is used for this purpose, it may be partly surrounded with a conical chimney, which steadies the flame considerably (Figs. 48, 49, 50). The supply of air, entering by the air-holes of the burner, should be so regulated that the inner blue flame is sharply defined, and the platinum wire should be held either in the blue point or just below it.

EXPERIMENT 31.—Heat a platinum wire loop, which is not more than an eighth of an inch (3 mm.) in diameter, in the inner blowpipe-

flame. If the wire is clean, it will become red hot without colouring the flame.

If the wire colours the flame, it must be boiled with hydrochloric acid in a test-tube and then rinsed with water. Or it may be wetted with strong hydrochloric acid, and then heated strongly in the blowpipe-flame until it no longer colours the flame. If the loop cannot be cleansed in this way, the end of the wire must be cut off, and a fresh loop must be formed.

Now dip the wire-loop into a little sodium chloride solution on a watch-glass, and remove it filled by a drop of the solution. Then hold the loop at the tip of the inner blowpipe-flame: the outer flame will be coloured *bright yellow*.

Repeat the experiment, placing the loop containing the solution in the outer part of the Bunsen-flame about one-third from the top. The same yellow tint will be seen above the loop.

This yellow coloration is given to the flame only by sodium and by its volatile compounds. On looking at it through the indigo-prism (1369), no yellow coloration will be visible.

EXPERIMENT 32.—Remove all the sodium chloride from the platinum wire loop by heating it strongly in the tip of the blowpipe-flame as long as it imparts any colour to the flame. Then dip the wire-loop into some solution of pure potassium nitrate. This will impart to the flame a *pale lilac* colour, which is characteristic of potassium and its compounds. When this coloration is viewed through the indigo-prism it will appear *crimson*.

EXPERIMENT 33.—Now dip the wire loop into a mixture of a few drops of the sodium chloride solution with a few drops of the potassium nitrate solution, which has been made on a watch-glass. When the loop is held in the flame the sodium coloration only will be seen. But if this coloration is then viewed through the indigo-prism, the crimson potassium coloration will be seen distinctly. By means of the indigo-prism the potassium coloration is therefore discoverable, even when it is concealed by that of sodium.

THE SPECTROSCOPE.

63. **The Spectra furnished by the Spectroscope** afford the most certain means of detecting substances by means of their flame-colorations, more especially when the colorations due to several substances are mingled in the flame.

After the coloured light from the flame-coloration has passed through the slit of the spectroscope, it is separated into its constituent colours by traversing a glass prism.

The coloured bands or lines, which are seen as the result of this

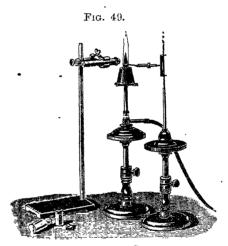
separation, are termed the *spectrum* of the substance. By their colours and relative positions they serve to identify the substance with certainty: and this is true whether the flame-coloration is produced by one substance only or by several, since the constituent colours are seen without interference one with another.

Two forms of spectroscope are in common use for chemical analysis.

The Direct-vision Spectroscope, which is shown ready for use in Fig. 66, is recommended by its compactness and its portability. In its smallest form it can be carried in the waistcoat pocket.

The Table Spectroscope, shown in Fig. 50 (page 48), is, however, to be preferred for general use as a stationary piece of apparatus in the laboratory.

The light enters each of these instruments through a slit, the width of which can be adjusted to suit strong or feeble flame-colorations. The rays of light, after passing the slit, are rendered less divergent by traversing a lens, and then pass through one or more prisms. The rays are finally focussed by means of a sliding eye-piece, so as to give a sharp image of the slit.

FIG. 49.

THE DIRECT-VISION SPECTROSCOPE.

Note.—Spectroscopic observations should be made by looking at the flame against a black background: a piece of black velvet hung behind the flame serves well for this purpose. It is also advantageous to check in other ways the admission of extraneous light into the slit. Delicate observations should therefore be carried out in a more or less darkened room; but in ordinary analytical work the spectroscope may be used on the working bench in the laboratory.

64. **The Direct-vision Spectroscope** may be held by the fingers, or if it is not provided with its own stand, it may be supported in a clamp in front of the flame (Fig. 49).

The slit is then slightly opened, and the eye-piece is adjusted until the vertical yellow line is sharply focussed. This line is always visible and is due to the sodium compounds present in the atmospheric dust which enters the flame.

If the spectroscope is held in the hand, it may be readily

focussed, before it is directed on the flame, by rendering sharp the dark Fraunhofer lines, which are seen on looking through a window at ordinary daylight.

More elaborate forms of the direct-vision spectroscope are available than that shown in Fig. 66. Most of these possess a scale for registering and mapping the position of the spectrum lines. If such an instrument is in common use, it is advisable to make out a spectrum chart, for purposes of reference, by the procedure which is described in paragraph 66.

Proceed to Experiment 34, attending to the *Note* (63).

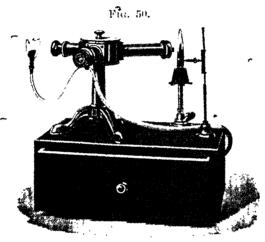



FIG. 50.

THE TABLE SPECTROSCOPE.

65. The Table Spectroscope (Fig. 50) has usually three brass tubes. One of these carries the adjustable slit, another the eye-piece, and the third a transparent photographic scale.

The instrument is brought into adjustment by placing a Bunsen-burner with closed air-holes in front of the slit (*Note*, 63). On looking through the eye-piece at this luminous flame, a "continuous spectrum" of unbroken colours will be seen. The upper and lower edges of this spectrum must be sharply focussed by moving the eye-piece, and the two tubes then arranged at such an angle as to give the longest complete spectrum possible. The tubes must either be permanently clamped in this position, or they must be so marked that they can at any time be easily brought into the same position with certainty.

Air is then admitted into the Bunsen-flame by opening the holes of the burner, and the yellow sodium line, which is always visible, is brought into a vertical position if necessary by rotating the slit-tube: the line is then sharply focussed.

The luminous flame is now lighted opposite the end of the scale-tube, the scale is focussed, and the scale-tube is shifted until the yellow sodium-line stands at a particular graduation; the fiftieth graduation has been selected for the special chart in Fig. 51.

This yellow line will usually be seen in all the following experiments, since it is derived from the atmospheric dust, which enters

the flame. It may be produced, if necessary, with greater intensity by introducing a platinum wire, moistened with sodium chloride solution, into the flame.

EXPERIMENT 34.—When the spectroscope has been brought into adjustment, the student should proceed to introduce a mounted platinum wire (14) into the front of the Bunsen-flame, at a level just below the slit of the spectroscope. The platinum wire loop should be moistened successively with solution of sodium chloride, potassium chloride, barium chloride, strontium nitrate and calcium chloride.

The wire may be conveniently supported in the flame by slipping its glass handle upon a horizontal wire arm, the height of which is adjustable on the stand represented in Figs. 49, 50.

Coloured vertical lines will be seen when these flame-colorations are observed through the spectroscope. These lines will always be the same in colour and position for the same flame-coloration. They will vary, however, in these respects with the colorations of different substances. A particular "line-spectrum" is therefore characteristic of each of the vapours which give rise to the above flame-colorations.

66. The Spectrum-chart.—The small pocket-spectroscope is not usually furnished with a graduated scale for measuring the position of the spectrum-lines. In the absence of a scale the relative positions of the lines of any particular spectrum may, however, be jotted down or remembered with approximate accuracy. Since the yellow sodium line is never absent, it will furnish a useful landmark in the spectrum.

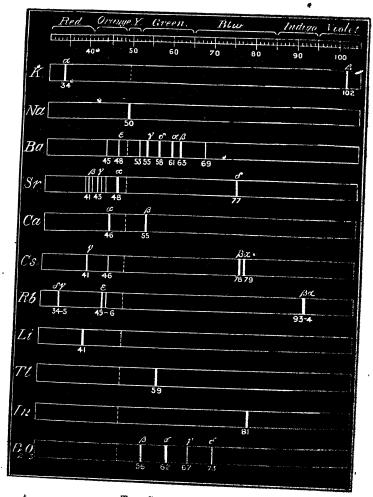
The scale of the larger spectroscopes, however, enables the position of the spectrum-lines to be noted down on a chart, and they are thus easily identified if the instrument is in adjustment. The instrument must always be brought to precisely the same adjustment as it possessed when the lines were mapped down in the spectrum-chart, if the chart is to be of any use.

The spectrum-lines will vary in position in different instruments, owing to variation in adjustment, and to difference in the material and angles of the prisms. Hence it is necessary to make a separate chart for each spectroscope.

The accompanying spectrum-chart (Fig. 51, p. 50) indicates a convenient method of mapping the lines, but the position of the lines on the scale only applies to the spectroscope from which this chart was made.

In the chart the relative intensity of the spectrum-lines may be inferred from their varying thickness, while the relative intensity

of the lines in each spectrum is indicated by the Greek letters applied in the order of decreasing intensity.

FIG. 51.

THE SPECTRUM-CHART.

The colour of each line is shown by the name of the colour, which is placed at the top of the chart over the region in which the line occurs. The position of each line is indicated by placing b it the number of the scale-graduation at which i

reasons which have been already stated, and it therefore serves as a landmark.

A chart of this kind must be at hand for reference when the spectroscope is used for analytical work. The spectrum-lines may be marked in with pen or pencil on a white ground, but they are more striking if coloured. The chart may conveniently be suspended near the instrument.

The spectrum of an unknown substance may also be identified, even when the instrument has not been carefully adjusted, and in the absence of the chart. For this purpose the position of the lines is noted on the scale and the flame-coloration of a known substance, which is believed to correspond to the spectrum which is under observation, is then thrown into the spectroscope. If the spectrum-lines of the unknown substance are identical in colour and in position with those given by the known coloration, the two spectra must be due to the same substance, and the unknown substance is therefore identified.

EXPERIMENT 35.—The student should carefully observe and map the spectra of several of the metals, which are shown in the spectrum-chart (Fig. 51). He should then proceed to examine some of the mixed spectra, which are obtained from solutions containing the salts of two or more of these metals. The ease with which many metals can be found by means of the spectroscope, even in the presence of one another, will thus become evident.

The Delicacy of this Method of detecting certain metals is extreme. Thus it is only in air which has remained undisturbed for a long time and is almost absolutely free from dust particles, that the sodium spectrum is not obtained from a Bunsen-flame. By using extremely dilute solutions of metallic salts, the delicacy of the method has been proved in the case of other metals. Bunsen states that one three-thousand-millionth of a grain of sodium can be detected by the spectroscope.

In the more Powerful Spectroscopes several prisms are used, and the lines of the spectra become more widely separated. Their relative positions are noted with great precision by moving the observing-tube until each line in succession is brought into the middle point of the cross-wires in the eye-piece. The position of the eye-piece is then read off on the graduated edge of the circular table on which the prisms stand, and registers the position of each line. Instruments of great power and precision are, however, not requisite for ordinary analytical work, and the simple form of table-spectroscope which has been already described will be found to be sufficient for the purpose.

67. Use of the Spectroscope in Chemical Analysis.—The spectroscope is of special use in chemical analysis for the following purposes :—

1. For readily detecting metals when their flame-colorations

are concealed by that of sodium; and generally for detecting metals, when their colorations are mixed in the flame.

2. For distinguishing similar colorations from one another. Thus the red coloration of strontium is easily distinguished from that of calcium and of lithium, by the strongest red line in each of the spectra being at a different distance from the sodium line; these very similar flame-colorations are further distinguished by the appearance of a characteristic blue line in the spectrum of strontium, and by a characteristic green line in the spectrum of calcium.

3. For detecting minute traces of many metals, which could scarcely be discovered by other means. The metals lithium, indium, thallium, rubidium, and cæsium were discovered by their spectra; and as these metals usually occur in minute proportion only, they are most conveniently detected by the spectroscope.

It is by no means a matter of indifference which compound of a metal is selected for obtaining the flame-coloration or spectrum of the metal. The most volatile salts are generally the chloride, the nitrate, and the chlorate; these accordingly give the most vivid but the least durable spectra. The coloration is increasingly feeble with the sulphate, the carbonate, and the phosphate; and the silicate does not usually give any coloration at all.

The coloration becomes more intense when the finely powdered substance is moistened with strong hydrochloric acid. But in the case of a silicate it is usually necessary to moisten the powder with hydrofluoric acid, or to mix it with pure ammonium chloride and calcium carbonate, before it is introduced into the flame.

Some very volatile substances give only a momentary flash of colour in the flame; while others, which are far less volatile, colour the flame only at the highest temperature obtainable. Hence careful observation of the flame-coloration through the spectroscope is necessary, from the moment that the substance is introduced into the flame, until the wire-loop has been heated to whiteness for some time.

The width of the slit of the spectroscope should be regulated according to the intensity of the lines to be looked for. A bright line can be observed with a narrow slit, and its position is thus noted with great precision. The slit must, however, be opened much more widely to see a faint line, such as Kβ (Fig. 68). It is undesirable that the lines should be of great breadth, since breadth prevents the position of lines on the scale from being accurately noted, and may even cause the edges of neighbouring lines to overlap.

PART II

ANALYTICAL REACTIONS

INTRODUCTORY REMARKS.

80. Object and Method of Chemical Analysis.—The study of chemistry has revealed the fact that every substance consists either of one kind of matter only, or of two or more different kinds.

Those substances which contain only one kind of matter are called "Chemical Elements." Their number at present amounts to about eighty. A list, which comprises most of them, is given at the end of the book (1420).

These elements do not usually occur singly. Two or more of them are commonly found together either in a state of mixture, or united in a more intimate manner in a "chemical compound."

It is the object of analytical chemistry to discover what element, elements, or sometimes what groups of elements or "radicles," any substance of unknown composition contains. But an analysis may also be undertaken in order to ascertain whether any particular element or group of elements is present in a given substance.

An analyst should be acquainted with the properties of each element and of the compounds which it forms with other elements. Efficiency in chemical analysis therefore presupposes a knowledge of what is usually termed Descriptive or Theoretical Chemistry.

For ordinary analytical purposes, however, certain marked properties or changes of each element, or group of elements, are selected; and by these properties, called "tests" or "reactions," its presence is detected.

Substances, which are added for analytical purposes, are called "reagents." Some reagents serve for detecting one element or compound only, and are therefore called "special reagents"; others separate or detect a group of elements or compounds, and are called "group reagents" or general reagents.

Two classes of reactions are employed in qualitative analysis :—

(1) "Dry Reactions" which are applied in the solid state. Some dry tests have been already described. As a rule these tests are more limited in their application and less delicate than the wet reactions, but since they do not require elaborate or fragile apparatus, they can be applied when a laboratory is inaccessible. Dry tests are therefore commonly used when one is prospecting for minerals and ores in comparatively remote places.

(2) "Wet Reactions."—The reactions usually employed in chemical analysis are, however, applied in solution, since wet tests are usually more delicate, and more generally applicable.

A short account of theoretical considerations involved in the use of wet reactions is given below.

81. Analytical Components of Dissolved Substances.—Salts, acids and bases, when in solution, do not behave as complete molecules, but as if they have been resolved into simpler components termed "ions."

Thus when hydrochloric acid (HCl) is dissolved in water, it is largely resolved into H-ions and Cl-ions. A similar "ionisation" occurs in the case of other soluble acids; and it is generally true that the solution of a compound, which produces H-ions when it is dissolved in water, gives an acid reaction to litmus.

The solution of an alkali, such as potassium hydroxide (KOH), contains the ions K and OH, the latter being the ion which gives the alkaline reaction to litmus.

The extent to which the molecules of an acid or base undergo ionisation when they are dissolved varies considerably with different substances and solvents. Strong acids, such as hydrochloric sulphuric and nitric acids, when they are dissolved in water undergo a high degree of ionisation ; whereas weak acids, such as carbonic nitrous and boric acids, are only slightly ionised by water. Similarly the powerful bases, potassium and sodium hydroxides, exist in aqueous solution largely in an ionised condition ; whereas the weaker ammonium hydroxide is ionised in water to a much smaller extent.

The solutions of many salts, such as potassium chloride (KCl), are neutral to test papers, since their solutions contain neither H (acid) nor OH (basic) ions. These salts may usually be produced by the action of the powerful acids upon the strong bases.

A large number of salt solutions, however, change the colour of test papers ; the majority of them showing an acid reaction, and a lesser number yielding an alkaline reaction. In these solutions the acidity and alkalinity are due to H and OH ions, which have been produced by a further reaction termed "hydrolysis." The solution

of a compound formed by the reaction of a strong acid upon a weak base usually gives an acid reaction, whereas the solution of the compound similarly produced from a weak acid and a strong base usually gives an alkaline reaction.

For a fuller explanation of the theory of ionisation the student is referred to works on chemical theory.

Assuming that the resolution into component ions occurs when salts are dissolved in water, the general applicability of the test for an element or radicle to a series of salts becomes intelligible. Thus a solution of any salt of calcium will give a white precipitate of calcium carbonate with ammonium carbonate, since the metal is separated by solution and acts independently of the other portion of the salt. Similarly any soluble metallic chloride will give a white precipitate with silver nitrate solution, because the ionised acid or chloride portion of the salt acts independently of the metal.

The systematic name of a salt or acid is given in accordance with the above considerations and consists of the name of the metal or hydrogen which the compound contains, associated with the name of the element or radicle with which the metal or hydrogen is combined.

Thus in the case of sodium sulphate, the name of the metal "sodium" is associated with that of the "sulphate" acid-radicle, and when this salt is dissolved in water the ions present in solution are Na and SO_4. The latter portion of the name of such a chemical compound usually denotes an acid-radicle, but occasionally denotes hydroxyl or oxygen or some other element.

Similarly acids are frequently called hydrogen salts, because hydrogen is united with the acid-radicle in acids, such as HCl, H_2SO_4, H_3PO_4, just as a metal is united with the acid radicle in salts, such as KCl, $MgSO_4$, Na_3PO_4. The acid-radicles in the above cases would be Cl, SO_4 and PO_4 respectively. Salts are also known in which both metal and hydrogen are combined with the same acid-radicle, such as $NaHSO_4$ or Na_2HPO_4; these are usually called "acid salts."

From the above examples it will be seen that some of the acid-radicles are elements, whilst most of them are "compound radicles." The above division of the name of a chemical compound, generally corresponds to the portions of the compound substance which are separately detected during its analysis. For analytical purposes substances are accordingly classed as *Metals* and *Acid-radicles*.

Certain elementary and compound substances cannot, however, be included in this generally useful classification; and certain non-metallic or metalloidal substances, as well as certain acid-radicles, are for analytical purposes conveniently classed with the metals.

82. Analytical Groups.—The metals are separated, by their behaviour with certain general reagents, into five principal Groups, and two of these Groups are further subdivided into two Subgroups. This classification is tabulated on the opposite page.

Each Group receives a distinctive name, which is derived either from its place in the system, or from some conspicuous or important member of the Group, or from the general reagent which is used to precipitate the Group. Thus we speak indifferently of the Fourth Group, of the Barium Group, or of the Ammonium Carbonate Group.

It is perhaps well to avoid referring to a Group by its number, since different analysts number the groups differently, and the number may not therefore denote the Group with certainty.

As will be noted later on (462), the acid-radicles cannot be as satisfactorily grouped for analytical purposes as the metals, since they do not usually undergo complete precipitation in groups the members of which admit of being subsequently separated from one another.

TRYING AND RECORDING THE ANALYTICAL REACTIONS.

83. In order to become fully acquainted with the behaviour of different substances with reagents, and thus to be able to detect these substances by their reactions, each of the reactions should be tried with the substance itself or with one of its compounds. The appearances which are presented are carefully observed and remembered, and the substance may then be easily recognised in a body of unknown composition by means of these reactions or tests.

The addition of a reagent to a substance causes some important and visible change to occur. This may be simply a change of colour, but it very usually consists in the formation of a precipitate or insoluble substance in the solution. The colour, the appearance, or the behaviour of this precipitate with other reagents, is characteristic of a particular element or compound-radicle.

As soon as a reaction has been satisfactorily performed, it should be briefly described in the notebook in a neat and concise manner. The nature of the chemical change which has occurred should then be explained by means of a chemical equation. Generally the use of chemical symbols and formulæ instead of chemical names may be adopted for purposes of brevity, and the use of the following abbreviated formulæ and words will also be advantageous.

ANALYTICAL CLASSIFICATION OF THE METALS.

GROUP I.	GROUP II.		GROUP III.		GROUP IV.	GROUP V.
Metals whose chlorides are insoluble in water and in dilute acid, and which are therefore precipitated from their solutions by hydrochloric acid :—	Metals whose sulphides are insoluble in dilute acid, and which are therefore precipitated from *acid* solutions by hydrogen sulphide :—		Metals which are precipitated by ammonium hydroxide as hydroxides from their solutions containing ammonium chloride, or as sulphides or hydroxides when ammonium sulphide or hydrogen sulphide is subsequently added :—		Metals whose carbonates are precipitated by ammonium carbonate in the presence of ammonium chloride :—	Metals whose solutions are not precipitated by any of the foregoing group-reagents in the presence of ammonium chloride :—
Hydrochloric Acid, or Silver Group :	**Hydrogen sulphide Group :**		**Ammonium hydroxide and Ammonium sulphide Group :**		**Ammonium carbonate, or Barium Group :**	**Potassium Group :**
	GROUP II.A. **Copper Group.** Sulphides insoluble in NaOH and in Am_2S :	GROUP II.B. **Arsenic Group.** Sulphides soluble in NaOH and in Am_2S :	GROUP III.A. **Ammonium hydroxide, or Iron Group :**	GROUP III.B. **Ammonium sulphide, or Zinc Group :**		
[Lead . . . Pb] Silver . . . Ag Mercurosum . Hg·	Mercuricum Hg·· [Lead . . Pb] Bismuth . Bi Copper . . Cu Cadmium . Cd	Tin . . . Sn Arsenic . . As Antimony . Sb	Aluminium . Al Iron . . . Fe Chromium . Cr	Zinc . . Zn Manganese . Mn Nickel . . Ni Cobalt . . Co	Barium . Ba Strontium . Sr Calcium . Ca	Ammonium NH_4 Potassium . K Sodium . . Na Magnesium Mg Lithium . Li

By adding each of these Group-reagents in the above order to the filtrate or clear solution from the preceding Group-precipitate, the metals in solution may therefore be separated from one another into five groups.

Lead will be found both in Groups I. and II., since its chloride is somewhat soluble.

84. Abbreviations employed for Entry in the Notebook.—For convenience in hasty writing, it is not uncommon to employ abbreviated formulæ for the compound radicles. This is more especially the case with those radicles which are constantly met with, and with those which have a complex composition. Only such abbreviations are employed in the text as save the use of brackets or of numbers. Thus Am_2 is short for $(NH_4)_2$, and Cy_2 for C_2N_2 or $(CN)_2$.

The following abbreviations may be used :—

Am for (NH_4), the metallic-radicle ammonium.
$\overline{T}$,, $(C_4H_4O_6)$, the acid-radicle of tartrates.
$\overline{A}$,, $(C_2H_3O_2)$, the acid-radicle of acetates.
$\overline{Ci}$,, $(C_6H_5O_7)$, the acid-radicle of citrates.
Cy ,, (CN), the acid-radicle in cyanides.

The following contracted words may also be used :—

expt.	for	experiment.	*insol.*	for	insoluble.
pp.	,,	precipitate.	*solⁿ.*	,,	solution.
ppⁿ.	,,	precipitation.	*cryst^{ne}.*	,,	crystalline.
pp^d.	,,	precipitated.	*colⁿ.*	,,	coloration.
sol.	,,	soluble.			

85. Example of Entry of Reactions in the Notebook.—The following example, selected from paragraphs 108–113, will serve as a specimen of the brief entry of reactions in the Note-book.

SILVER.—Used $AgNO_3$-solution.

Test.	Observation.
108. HCl	White pp., became curdy when heated; sol. in AmOH and in KCN, and repp[d] on adding HNO_3 in excess; insol. in hot HNO_3; darkened by exposure to light: $HCl + AgNO_3 = AgCl + HNO_3$.
109. K_2CrO_4 . . .	Deep crimson pp.: $K_2CrO_4 + 2AgNO_3 = Ag_2CrO_4 + 2KNO_3$.
112. AmOH . . .	Light brown pp. on adding a little dilute AmOH, easily sol. in excess :— $AmOH + AgNO_3 = AgOH + AmNO_3$.
113. Mixed solid with Na_2CO_3 and heated on charcoal in the inner blowpipe-flame.	White metallic bead obtained, which was malleable but did not mark paper: no incrustation formed.

GENERAL RULES FOR WORKING.

86. The student should attend carefully to the following precautions. They will materially aid the progress and accuracy of his work, and if they are observed from the commencement they will not be felt irksome.

1. Before beginning work, look through the reagent-bottles belonging to the working bench (1409). Replace any which are absent, and see that the bottles are arranged in a convenient order. Then proceed to fill any which are empty, and to relabel any whose labels are imperfect or loose.

2. Arrange the apparatus, which is required for use, on the back part of the bench, so as to leave the front of the bench free to work upon. This will lessen the risk of upsetting anything. (See Fig. 66, p. 331.)

3. All dirty glass and porcelain, which is not in use, should then be carefully cleansed. This ought, however, to be unnecessary, since apparatus should never be put away dirty.

4. When a reagent-bottle is to be used, take it in the right hand; remove the stopper by grasping it between two of the fingers, or between the fourth finger and palm of the left hand; hold the stopper in this way while the bottle is being used; then replace it immediately, and return the bottle to its place. Do not lay down the stopper on the bench.

5. Pour a liquid reagent out of the side of the bottle opposite to that which bears the label; and prevent the last drop of the liquid from running down the outside, by touching the lip of the bottle either with the stopper, or against the clean edge of the vessel.

6. Solid reagents should be taken out of the bottle on a clean knife-blade or spatula, or with a slip of clean cardboard or paper.

7. Each bottle must be restoppered and replaced on the shelf, in its proper place and with the label outwards, immediately after use; it must never be left standing on the working-bench.

8. If a solution or precipitate has to be put by for some time before it undergoes further examination, it should always be labelled. A piece of gummed paper may be attached to it, bearing either an inscription, or a reference number which is explained in the note-book and which is sufficient to recall to mind what the solution or precipitate consists of. It is well never to trust to memory in this matter.

It will be found to be unadvisable as a rule to leave a precipitate thus, since it is apt to dry or to undergo oxidation.

9. It should be remembered that if metal crucible-tongs are employed for holding hot evaporating basins containing acids, some of the metal is apt to be dissolved and thus introduced into the solution. A hot dish may be moved either by holding it with a cloth, or by lifting the stand upon which the dish is placed.

10. Liquids only should be poured down the sinks. All solid refuse, such as soiled filters, broken glass, and pieces of charcoal, should be thrown into a receptacle which is placed in an accessible position.

11. When a substance is being examined in order to find out its composition, the student should fully write down in the note-book each test or process, with the result obtained, as soon as it is completed. The analysis is thus written out gradually as it progresses. On no account should the entry of the results be left until the completion of the analysis.

This rule cannot be too strongly enforced, as neglect of it always causes uncertainty and confusion. The most convenient form of entry is that of the Analytical Tables.

12. Cleanliness and neatness in analytical work cannot be too carefully attended to. More confusion and error may be caused by using dirty test-tubes, beakers, dishes, and funnels, than would be thought possible by the beginner. Work should also be rendered as systematic as possible, in order to economise time and thought.

87. Directions for Trying the Analytical Reactions:—

1. A solution of the substance, the reactions of which are to be tried, must always be employed unless it is specially stated that the solid is required. The solid substance is usually only required for blowpipe reactions.

A solution may be kept in readiness, or it can be easily made by warming the solid with water or with dilute acid (1411-1413).

2. Pour into a test-tube or small beaker about twenty cubic centimetres (20 c.c.) of the solution of the substance: this constitutes the "original solution." If the solid substance is also required, take some of it upon a watch-glass and powder it finely.

3. Pour about 2 c.c. of the original solution into a perfectly clean test-tube and add the first-mentioned reagent. A few drops only of the reagent should be added at first, more can be gradually added afterwards if necessary.

The habit of working with small quantities both of solutions and of reagents must be acquired from the first.

In trying each of the reactions a separate portion of the original solution is to be taken.

4. Before trying a reaction, the student should carefully read through the whole of the description of the results to be obtained. The experiment is then to be performed, literally following out the directions given.

It is a necessary condition of after success that each result should be obtained precisely as is stated in the text. The student must never on any account pass on without being satisfied that the statements of the book are true, and that he could at any time repeat the test successfully.

5. The water used for the tests and reactions must always be distilled water.

The acids are to be used in a dilute condition, unless it is stated that the strong acid is to be employed.

In all cases KOH and NaOH may be used indifferently the one for the other.

SECTION III

REACTIONS FOR THE METALS

Introductory Remarks.

99. Paragraphs which are printed in small type may be passed over or simply read through if time is limited; they should, however, receive careful attention from the general analyst.

Since chemical symbols and formulæ are freely used in the text, both the name and the symbol or formula for each reagent are given in the following reactions when the reagent is first mentioned; subsequently the chemical formula only is used. Any difficulty in connecting symbols and formulæ with chemical names should also be prevented by referring to the tables giving the names and corresponding symbols of the chemical elements (1420), the formulæ of minerals containing them (1419), and of the substances used for analytical purposes (1409–1418).

The list of minerals containing the more commonly occurring metals (1419) furnishes information as to the compounds in which these metals occur in nature, and also indicates by formulæ the chemical composition of these natural compounds.

The chemicals and reagents required for the work of Parts II and III of the book will be found tabulated in Part IV (1407–1414), where also their preparation is described (1383–1400).

Occasionally non-metallic or metalloidal elements are associated with the Metal Groups for the purpose of analytical classification.

The reactions of the Rarer Metals belonging to each Group are entered in small type at the end of the Group.

GROUP I.—SILVER GROUP.

100. This Group includes Pb, Ag, Hg', together with the rarer elements Tl and W.

The solutions of Pb, Ag, Hg', Tl differ from those of all other metals, by being precipitated as chlorides by hydrochloric acid (HCl) or by a dissolved chloride. Since, however, lead chloride ($PbCl_2$) and thallium chloride (TlCl) are somewhat soluble in water, these metals are not entirely precipitated in this Group as chlorides, and they will also be found in Group II.A. as sulphides in the course of analysis. W is precipitated as H_2WO_4 by HCl.

For the Rarer Elements in this Group refer to paragraphs [illegible]–131.

Lead (Pb).

Density 11·37, melting point 327·4° C.

101. Lead is a bluish-white metal, which slowly tarnishes in the air, and is so soft that it may be indented with the finger nail, and will readily yield a streak on paper. It is insoluble in dilute sulphuric and hydrochloric acids, but dissolves in nitric acid with the evolution of nitric oxide.

Lead forms the following well-known oxides, lead monoxide (PbO) yellow, red lead (Pb_3O_4), and lead peroxide (PbO_2) brown.

The lead salts correspond to the monoxide. The lead-ion is divalent and colourless.

For lead-minerals refer to par. 1419.

REACTIONS OF LEAD.

Use Lead acetate, $Pb\bar{A}_2.3H_2O$, dissolved in dilute acetic acid.

102. **Hydrochloric acid (HCl)**: white precipitate ($PbCl_2$) which forms only in cold and strong solutions. Boil the precipitate with sufficient water: it will dissolve, but the $PbCl_2$ will separate again in slender crystals, when the hot solution is slowly cooled.

103. **Hydrogen sulphide (H_2S)**: black precipitate (PbS). This precipitate is often red if much hydrochloric acid is present in the solution; but the red colour changes to black when water is added and H_2S is passed, or when H_2S-water is added.

Filter, and show with separate portions of the precipitate that PbS is insoluble in potassium hydroxide (KOH) and in ammonium sulphide (Am_2S), but is soluble in boiling dilute nitric acid (HNO_3); also that it is converted by boiling strong HNO_3 into white insoluble $PbSO_4$.

104. **Sulphuric acid (H_2SO_4)**: white precipitate ($PbSO_4$). This precipitate is much less soluble in dilute H_2SO_4 and in alcohol than in water; hence the dilute H_2SO_4 should be added in excess to a pretty strong solution of the lead salt.

Shake up the liquid, and pour it off into two test-tubes; let the liquid stand in each of these tubes and decant it from the precipitate (42). Show that the precipitate may be dissolved by boiling it either with ammonium acetate ($Am\bar{A}$) solution, or with acetic acid ($H\bar{A}$) after adding ammonium hydroxide ($AmOH$) in excess; show also that it dissolves in boiling strong HCl.

105. **Potassium chromate (K_2CrO_4)**: yellow precipitate ($PbCrO_4$). Pour off the liquid with the precipitate into two tubes,

and show that the precipitate is soluble in KOH, but insoluble in HĀ.

106. **Blowpipe-test on Charcoal.**—Mix some powdered lead acetate with about twice as much powdered sodium carbonate (Na_2CO_3) in a cavity on a piece of charcoal, and heat the mixture in the inner blowpipe-flame (Exp. 28, 60).

A yellow incrustation will form upon the surface of the charcoal around the mixture, and small lustrous globules of Pb will be seen within the cavity. The incrustation is readily removed by heating it in the inner blowpipe-flame, and it colours the flame meanwhile pale blue, unless this colour is masked by the sodium yellow.

Detach one of the metallic globules with the point of a pen-knife, place it on the flat bottom of an inverted mortar, and strike the globule a blow with the pestle. It will flatten out without cracking or breaking into powder, showing that Pb is *malleable* and not *brittle*.

If one of the cleansed globules is fixed upon the point of a pen-knife, and is then rubbed with gentle friction on paper, it will mark the paper as a blacklead pencil does.

Silver (Ag).

Density 10·47, melting point 960° C.

107. Silver is a white lustrous metal; it is highly malleable and ductile, and is not affected by air unless hydrogen sulphide is present, when it is blackened by the formation of silver sulphide.

Silver is insoluble in hydrochloric acid, but dissolves readily in nitric acid and in hot concentrated sulphuric acid. One series of salts of silver is known, which correspond to the monoxide (Ag_2O). The silver-ion is monovalent and colourless.

For silver-minerals refer to par. 1419.

REACTIONS OF SILVER.

Use Silver nitrate, $AgNO_3$.

108. **HCl**: white precipitate (AgCl), which when it is shaken or heated.

Pour off the liquid with the precipitate into four test-tubes. Filter one portion, then wash the precipitate and let it stand for some time exposed on the filter to sunlight or to common daylight; it will become blackish-purple.

Show with the other portions that AgCl dissolves readily when it is heated with AmOH or with potassium cyanide (KCN)-solution,

and is precipitated again from these solutions when HNO_3 is added in excess. Show also that AgCl is insoluble in HNO_3, even when the acid is boiled.

109. **K_2CrO_4 :** deep crimson precipitate of silver chromate, Ag_2CrO_4.

110. **H_2S or Am_2S :** black precipitate (Ag_2S), insoluble in Am_2S and in KOH, soluble in boiling dilute HNO_3.

111. **KOH :** brown precipitate (AgOH), insoluble in excess.

112. **AmOH :** light brown precipitate (AgOH), produced only when very dilute AmOH is added drop by drop, since AgOH is very easily soluble in excess of AmOH.

113. **Blowpipe-test on Charcoal.**—If any solid substance containing Ag is mixed with powdered Na_2CO_3 and the mixture is then heated on charcoal in the inner blowpipe-flame, white malleable globules or scales of Ag will be obtained, but no incrustation will be formed on the charcoal. The globules do not mark paper (106).

Mercury (Hg).

Density 13·6, melting point −39° C, boiling point 357° C.

114. Mercury is a silver-white liquid metal which remains unaltered in the air at ordinary temperatures.

The metal is insoluble in hydrochloric acid, but dissolves in hot concentrated sulphuric acid. Dilute nitric acid acts upon it slowly at ordinary temperatures, forming mercur*ous* nitrate: the concentrated acid acts rapidly, forming mercur*ic* nitrate, and coloured oxides of nitrogen are evolved.

Mercury forms two series of compounds: "mercurous compounds," corresponding to mercurous oxide Hg_2O, with a monovalent colourless metallic ion; and "mercuric compounds," corresponding to mercuric oxide, HgO, with a divalent colourless metallic ion.

The metal present in these two classes of compounds may be distinguished as "mercurosum" ($Hg^{\cdot}$) and "mercuricum" ($Hg^{\cdot\cdot}$) respectively.

Mercurosum and mercuricum have to be placed in different analytical groups, and their common reactions are not repeated in each group. The reactions which are given below are characteristic of mercurous salts and are distinctive of the two classes of salts, while those given under mercuric salts (134–136, 140 and 141) are common to both classes of salts.

Mercury occurs in nature as Cinnabar, HgS.

REACTIONS OF MERCUROSUM (Hg˙).

Use Mercurous nitrate, $Hg_2(NO_3)_2.H_2O$, dissolved in dilute HNO_3.

115. **HCl :** a white precipitate (Hg_2Cl_2), insoluble in cold dilute acids, but soluble when it is warmed with HNO_3 or with a mixture of HCl and HNO_3 which converts it into soluble mercuric chloride ($HgCl_2$).

This precipitate becomes black when AmOH is poured upon it, but does not dissolve: $Hg_2Cl_2 + 2NH_4OH = NH_2.Hg_2Cl + NH_4Cl + 2H_2O$.

A solution of mercuric salt is not precipitated by HCl or by solution of a chloride.

116. **AmOH, or KOH :** black precipitate, insoluble in excess. In a solution of mercuric salt AmOH yields a *white* precipitate (137), and KOH gives a yellow precipitate (138).

117. **Potassium iodide (KI) :** yellowish-green precipitate of Hg_2I_2, insoluble in excess.

In a solution of mercuric salt, KI produces a pink precipitate, which turns to scarlet, and is soluble in excess of either KI-solution or of mercuric solution.

DETECTION OF METALS IN GROUP I.

After the student has carefully worked through the reactions for metals in Group I., he should proceed to apply the knowledge which he has acquired to the detection of the metals belonging to this group, occurring either singly or together as is directed below.

118. **A solution, which is to be examined for Pb, Ag, and Hg˙,** is precipitated by adding HCl in excess (see *Note*) and the precipitate is examined by Table I. (125o).

Examination of a white solid for Metals of Group I.

The substance was dissolved in water, and dilute HCl was added in excess; the liquid was then filtered and the precipitate was washed several times with hot water, the washings being kept separate :—

Washings: a few white crystalline needles deposited on cooling.	**Residue**: rinsed with AmOH into a test-tube and boiled, then filtered :—	
Confirmed by adding K_2CrO_4, a copious yellow precipitate showed :—	**Filtrate**: added HNO_3 in excess, no white precipitate formed :—	**Residue** on the filter was black :—
Presence of Pb.	**Absence of Ag.**	**Presence of $Hg^{\cdot}$.**

Found Pb and $Hg^{\cdot}$.

REACTIONS FOR RARER ELEMENTS IN GROUP I.

120. The rarer elements included in this Group are Tl and W.

The addition of HCl in excess partially precipitates Tl as chloride, and completely precipitates tungstic acid from a tungstate.

Since TlCl is only partially precipitated in Group I., owing to its being somewhat soluble in water, Tl is also found in the ordinary course of analysis in Group III.B., where it is completely precipitated as sulphide by Am_2S.

THALLIUM (Tl).—Use Tl_2SO_4-solution.

121. Tl occurs in small quantity in many natural sulphides, and occasionally in the ashes of plants and in mineral waters. It is not a constituent of any characteristic mineral, and the principal source from which it is prepared is the dust which settles in the flues of the burners of sulphuric acid chambers, when pyrites is used in the manufacture.

Tl yields both thallic and thallious salts, but the former are very unstable, changing, even when their solutions are heated, into thallious salts.

122. HCl: a white precipitate (TlCl), which rapidly settles, does not blacken in the light, and is soluble in aqua regia. It is soluble in a large quantity of water, and therefore does not form in dilute solutions.

123. KI: a yellow precipitate (TlI), almost insoluble in water, but more soluble in KI-solution. If ferric salt is present in the solution, it must be reduced by H_2SO_3 before KI is added. This is the most delicate test for Tl.

124. H_2PtCl_6 (*Note*, 420): yellow precipitate (Tl_2PtCl_6), almost insoluble in water.

125. Am_2S: black precipitate, which is easily coagulated by heat; is insoluble in AmOH, in alkaline sulphides, and in KCN-solution; is readily oxidised by the air to Tl_2SO_4, and is easily soluble in mineral acids.

Tl is completely precipitated by H_2S from a solution in which $H\bar{A}$ is the only free acid present, but the presence of a free mineral acid prevents the precipitation.

126. Flame-coloration.—Thallium compounds impart to the Bunsen flame an intense *green* colour, which rapidly disappears.

The spectrum (Fig. 51, page 50) consists of one bright emerald-green line, and is very characteristic. Thallium may be easily detected by the spectroscope in solution, or in any of the precipitates which are mentioned above.

TUNGSTATE (WO_4).—Use Na_2WO_4-solution.

127. W usually occurs native in the form of a tungstate. An insoluble tungstate yields a soluble alkaline tungstate when it is fused with an alkaline carbonate. From the solution of an alkaline tungstate HCl precipitates the tungstic acid completely.

128. HCl, HNO_3, or H_2SO_4 : white precipitate of hydrated H_2WO_4 which becomes yellow and anhydrous when the liquid is boiled ; it is insoluble in excess of acid, but soluble in AmOH.

If a piece of Zn is dropped into the acid liquid containing the precipitate, it yields a deep blue colour by reduction of the tungstic acid to W_2O_5.

129. $SnCl_2$ in neutral solution, made by dissolving $SnCl_2$-crystals in water and filtering, gives a *yellow* precipitate, which becomes *blue* when HCl is added and the liquid is heated. This is a most delicate test for a tungstate.

130. Am_2S yields no precipitate in the solution of an alkaline tungstate ; but if Am_2S is added, and the liquid is then made acid with HCl, brown WS_3 is precipitated.

131. Microcosmic-bead : outer flame, *colourless or yellow* ; inner flame, *blue* ; if a little $FeSO_4$ is heated with the fused bead, the colour changes to *blood-red*. These colours are best seen when the bead is perfectly cold.

For the Detection of the Rarer Elements of this Group, refer to the first column in the Table (1323).

GROUP II.—COPPER AND ARSENIC GROUP.

132. This Group includes the metals $Hg^{\cdot\cdot}$, Pb, Bi, Cu, Cd, As, Sb, Sn, together with the rarer elements Pd, Os, Rh, Ru, Au, Pt, Mo, Se, Te, Ir.

The reactions of the rarer elements are given in paragraphs 210–261.

Group II. is subdivided into Groups II.A. and II.B.

GROUP II.A.—COPPER GROUP.

133. This Group includes $Hg^{\cdot\cdot}$, Pb, Bi, Cu, Cd, (Pd, Os.)

The compounds of these metals differ from those of the metals in Groups III.A., III.B., IV., and V. by being precipitated as sulphides by H_2S from their acid solutions. With the exception of Pb, which is partially precipitated from strong solutions as chloride, these metals are not precipitated from their solutions by HCl or by dissolved chlorides.

The precipitated sulphides of the metals of Group II.A. differ from those of Group II.B. by being insoluble both in Am_2S and in KOH.

H_2S does not precipitate the members of this Group from strongly acid solution readily or completely; these solutions must therefore be suitably diluted with water in order to ensure their precipitation.

Mercury (Hg).

A statement of the general properties of this metal and its compounds has already been given in paragraph 114.

It is also explained in that paragraph that mercury forms two classes of salts, the metal being termed mercuricum in the mercuric compounds which are classed in Group II.A., and mercurosum in mercurous compounds which are classed in Group I.

The reactions given in paragraphs 115–117 and 137–139 are distinctive tests for mercury in these two classes of salts.

REACTIONS FOR MERCURICUM ($Hg^{\cdot\cdot}$).

Use Mercuric chloride ($HgCl_2$).

134. **H_2S:** black precipitate (HgS). If the H_2S-solution is added slowly, the precipitate is first *white*, then *brown* or *orange*,

and ultimately *black*. These changes of colour, which are due to the formation of an intermediate compound ($HgCl_2.2HgS$), are characteristic of mercuric salts.

Filter off the precipitate of HgS, and wash it free from dissolved chlorides; then place portions of it in two test-tubes.

Boil one of these portions with strong HNO_3, the precipitate will not be dissolved; now add HCl to this portion and warm again, the precipitate will dissolve.

Boil the second portion with Am_2S, the precipitate will not dissolve.

Hence HgS is insoluble in hot strong HNO_3, and in Am_2S. It is, however, easily soluble in a mixture of HNO_3 and HCl, which is known as *aqua regia*.

135. **Stannous chloride, $SnCl_2$**; white precipitate (Hg_2Cl_2): if an excess of $SnCl_2$ is added, the white precipitate becomes grey; examination with a lens shows that the grey precipitate consists of small globules of Hg:—

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$$
$$Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4.$$

Boil the liquid, and decant it from the grey precipitate. Then heat the precipitate with strong HCl; the Hg-particles will usually unite to form larger globules, which are visible through a lens or even to the naked eye.

136. **Copper, Cu**: cleanse a small strip of copper sheet, or a copper coin, by rubbing it with emery-paper, or by dipping it into strong HNO_3. Immerse it in some $HgCl_2$-solution, which has been acidified by the addition of a few drops of HCl. The Cu will become coated with a grey film of Hg:—

$$HgCl_2 + Cu = Hg + CuCl_2.$$

Allow the Cu to remain immersed in the liquid for several minutes, then remove it, dry its surface, and rub it with a cloth or with a piece of wash-leather. The Cu will appear more or less whitened like silver, since the mercury has formed an "amalgam" with it.

The Hg may be readily driven off from the copper by heating it strongly. If the copper strip is heated in a test-tube, or better in a small glass tube sealed at one end (13), a sublimate of globules of Hg will form upon the cool sides of the tube.

137. **AmOH**: white precipitate of NH_2HgCl, insoluble in excess.

138. **KOH**: yellow precipitate of mercuric oxide (HgO).

139. **KI**: red precipitate of mercuric iodide (HgI_2), readily soluble in excess of either KI-solution or $HgCl_2$-solution.

140. **Mercury mirror.**—Dry some sodium carbonate perfectly by heating it strongly on platinum foil or in a porcelain dish. Also dry the interior of a small test-tube by heating it in the flame, and then sucking out the moist air by a glass tube, which has been pushed down to the bottom.

Mix *a little* finely-powdered $HgCl_2$ intimately with about four times its measure of the dry and finely-powdered $NaCO_3$. Then transfer the mixture into the tube and cover it with a layer of the dry Na_2CO_3.

Now cleanse the inside of the tube perfectly, and proceed to heat the upper layer of Na_2CO_3 strongly, gradually extending the heat to the mixture below, while the upper layer is maintained at a high temperature. Hg-vapour will be evolved, and will condense on the inside of the tube as a silver-white mirror.

Sometimes the globules of metal are so small that they appear as a grey film only, or they are few and scattered and are not easily visible. In either case the minute globules may usually be detected by means of a pocket-lens, or they may be united into larger and visible globules by rubbing the inside of the tube with a glass rod. Even very minute globules may be seen, when they have been flattened by pressing them with a glass rod against the inside of the tube.

Remarks.—The powder is most easily transferred to the tube, by alternately scooping it up with the mouth of the tube, and tapping the tube upon the table so as to shake the powder to the bottom.

Or the powder may be poured upon a narrow strip of notepaper, which has been folded over into a trough longer than the tube; the paper is then pushed into the horizontal tube, the tube is held erect and tapped, and the powder is thus easily transferred to the bottom of the tube without soiling the glass.

Both the inside of the tube and the powder must be perfectly dry, else particles will adhere to the inside of the tube and interfere with the detection of the metallic globules.

The heating must not be commenced until the inside of the tube is perfectly clean. It is cleansed, if necessary, by means of a twisted slip of filter-paper or with a wooden match.

If any drops of water condense on the inside of the tube during the first stage of the heating, they must be removed by a piece of filter-paper. If, however, proper care has been taken in drying the powder, no moisture will be evolved from it. The escape of steam or gases from the powder is very undesirable, as it is likely to sweep uncondensed mercury vapour out of the tube.

141. **Heat a little Solid $HgCl_2$** in a tube closed at one end; the substance will sublime in white fumes, showing that mercury compounds are volatile.

Bismuth (Bi).

Density 9·8, melting point 268° C.

142. Bismuth is a brittle, crystalline, white metal with a reddish tinge. It slowly oxidises superficially in the air. The metal is very slightly attacked by hydrochloric acid and by sulphuric acid, but is readily dissolved by nitric acid.

The bismuth salts correspond to the oxide Bi_2O_3 and the bismuth-ion is trivalent and colourless. Bismuth hydroxide, $Bi(OH)_3$, is a weak base, hence bismuth salts are partially "hydrolysed" water, forming insoluble basic salts.

For minerals containing Bi refer to par. 1419

REACTIONS OF BISMUTH.

Use Bismuth nitrate, $Bi(NO_3)_3.5H_2O$, dissolved in dilute HNO_3.

143. **H_2S :** brownish-black precipitate (Bi_2S_3) :—

$$2Bi(NO_3)_3 + 3H_2S = Bi_2S_3 + 6HNO_3.$$

Decant most of the liquid from the precipitate; then shake up the precipitate with the remainder, pour some of the liquid with the precipitate into three test-tubes, and show that the precipitate is insoluble in Am_2S and in KOH, but soluble in strong HNO_3.

144. **AmOH,** or **KOH :** white precipitate, $Bi(OH)_3$, insoluble in excess of the reagent. Pour off a small quantity of the liquid and precipitate into a test-tube, add much AmOH and warm: the precipitate will remain undissolved. Filter off the rest of the precipitate, and keep it for the reaction described in paragraph 146.

145. **Alkaline stannite :** add KOH-solution to $SnCl_2$-solution until the precipitate which forms at first is just redissolved, then add a few drops of the bismuth nitrate solution : a black precipitate of metallic bismuth will be formed.

146. **H_2O.**—Pour a few drops of boiling dilute HCl upon the precipitate which remained in the filter from par. 144, and allow the acid solution to drop from the funnel into a large quantity of distilled water. A *milkiness* will appear (*Note*), which is due to the formation of BiOCl :—

$$BiCl_3 + H_2O = BiOCl + 2HCl.$$

Pour some of the milky liquid into two test-tubes; add to one portion a little strong HCl and warm it, the precipitate will dis-

solve; to the other portion add $H_2\bar{T}$ and warm, the milkiness will remain, differing in this way from that caused by SbOCl (189).

Note.—If Bi is present in small quantity only, this milkiness will often not appear until the liquid has been stirred and then allowed to stand for a few minutes.

A similar precipitate ($BiONO_3$) may be obtained by allowing the original bismuth nitrate solution to fall drop by drop into much water, but the nitrate is less completely precipitated than the chloride by mixture with excess of water.

147. **K_2CrO_4**, or **$K_2Cr_2O_7$**, added after some strong $Na\bar{A}$-solution (*Note*), gives a yellow flocculent precipitate of basic bismuth chromate. When KOH is added, the precipitate will not dissolve, differing in this way from $PbCrO_4$; it will dissolve, however, completely when HCl or HNO_3 is added in excess.

Note.—The addition of $Na\bar{A}$ in the above reaction is necessary in order to replace the nitric acid in the original solution by $H\bar{A}$, since the precipitate is readily soluble in HNO_3, but is insoluble in $H\bar{A}$:—$Na\bar{A} + HNO_3 = NaNO_3 + H\bar{A}$.

148. **Blowpipe-test on Charcoal.**—Heat a mixture of powdered $Bi(NO_3)_3$ and Na_2CO_3 in a cavity on charcoal in the inner blowpipe-flame.

There will be seen around the cavity an incrustation which is *orange-red* while hot and *yellow* when cold. White globules of Bi will also be seen within the cavity; they are very brittle and will be easily crushed to powder by a blow with the pestle; they are too hard to mark paper (106).

Copper (Cu).

Density 8·9, melting point 1083° C.

149. Copper is a reddish-brown lustrous metal, which is soft, ductile and malleable. In ordinary air it becomes coated slowly, at ordinary temperature, with a green basic carbonate; if it is heated strongly in the air, a superficial coating of black oxide is formed.

Cold hydrochloric acid and sulphuric acid scarcely affect the metal; it is dissolved slowly by hot hydrochloric acid, and rapidly by nitric acid under all conditions. The metal is also rapidly attacked by hot strong sulphuric acid. Ammonia acts upon copper in the presence of air, forming a blue solution.

Copper forms two classes of compounds: the *cuprous* salts, corresponding to the red cuprous oxide, Cu_2O, contain the monovalent colourless ion, cuprosum; the *cupric* salts, corresponding to the black cupric oxide, CuO, contain the divalent bluish-green ion, cupricum.

The cuprous salts are white and insoluble in water, and they readily pass by oxidation in acid or ammoniacal solution into the blue cupric compounds; they are therefore not of common occurrence and are comparatively unimportant: a few distinctive tests only are given for them.

The cupric salts are of common occurrence and of considerable importance, their reactions are therefore described in detail. Their solutions are blue in colour.

For minerals containing Cu refer to par. 1419.

REACTIONS OF CUPROUS COMPOUNDS.

Use a solution of Cuprous chloride, Cu_2Cl_2, in dilute hydrochloric acid.

150. **KOH**: yellow precipitate of $Cu_2(OH)_2$: when the liquid is boiled the precipitate loses water and changes into red cuprous oxide (Cu_2O). The precipitate quickly absorbs oxygen when it is exposed to the air, and is converted into black cupric oxide, CuO.

151. **H_2S**: black precipitate of cuprous sulphide (Cu_2S): soluble in warm dilute nitric acid as blue cupric nitrate, with separation of sulphur.

152. **H_2O**: when the cuprous salt solution is poured into much water, insoluble white Cu_2Cl_2 is precipitated, and this gradually turns blue by oxidation when it is exposed to the air.

153. **The Dry Reactions** for cuprous compounds give results similar to those for cupric compounds (161–163).

REACTIONS OF CUPRIC COMPOUNDS.

Use Copper sulphate, $CuSO_4.5H_2O$.

154. **H_2S**: brownish-black precipitate (CuS): filter off the precipitate, keeping the funnel carefully covered with a glass plate, since CuS is quickly oxidised by exposure to the air, and the $CuSO_4$ thus produced dissolves and runs through in the filtrate.

Place some of the precipitate in five test-tubes and show that it is insoluble in KOH, in Am_2S and in boiling dilute H_2SO_4, but that it is soluble in boiling HNO_3 and in KCN-solution.

155. **AmOH**, if it is added in a diluted state and in very small quantity, gives a *greenish-blue* precipitate.

If more AmOH is added this precipitate dissolves, yielding an *intensely blue* liquid, which contains a cuprammonium compound, $Cu(NH_3)_4SO_4$.

156. **KOH** produces a pale blue flocculent precipitate of $Cu(OH)_2$ which is converted into black CuO when the liquid is heated.

157. **KCN-solution** : yellow precipitate, $CuCy_2$, which changes to white Cu_2Cy_2, and this dissolves in excess of the KCy-solution as colourless potassium cuprous cyanide, K_3CuCy_4.

This solution contains no copper-ion, and is therefore not precipitated by H_2S and by other reagents which precipitate cupric solutions. This property is made use of as a means of separating copper from cadmium (170,4).

158. **Potassium ferrocyanide, K_4FeCy_6** : reddish-brown precipitate (Cu_2FeCy_6), insoluble in $H\bar{A}$; the colour of this precipitate is best seen when the reaction is tried in a white porcelain dish. In a very dilute copper solution, only a reddish colour is seen at first when the ferrocyanide solution is added.

159. **Fe.**—Polish a piece of steel or iron wire or sheet, or the blade of a penknife, if necessary, by rubbing it with emery-paper, remove all grease by boiling it in a little dilute KOH-solution, then dip it into $CuSO_4$-solution, which has been acidified with a few drops of H_2SO_4; the immersed surface will be gradually covered with a red film of Cu.

160. **Zn and Pt.**—Place a piece of platinum foil or wire in some $CuSO_4$-solution, which has been acidified with H_2SO_4 in a porcelain dish or in a watch-glass, then drop a small piece of Zn upon the platinum: a red film of Cu will be deposited upon the platinum.

161. **Blowpipe test on Charcoal.**—If finely-powdered copper sulphate and Na_2CO_3 are mixed in a cavity on charcoal, and the mixture is then heated in the inner blowpipe-flame, red scales or globules of Cu are obtained. These are best seen after they have been washed by levigation (61). The addition of solid KCN facilitates the smelting process, and often enables globules of copper to be obtained.

162. **A Borax-bead containing Cu** is *green* while hot and *blue* when cold, after it has been fused in the outer blowpipe-flame.

Fusion in the inner blowpipe-flame causes the bead to become *red*; it may even become *colourless*, if very little Cu is present and the bead is long heated in a good reducing flame: the introduction of a minute fragment of Zn or Sn into the bead aids this change.

163. **Flame-coloration.**—If a loop of platinum wire is dipped into $CuSO_4$-solution and is then held in the inner blowpipe-flame or in the Bunsen-flame, it imparts a *green* coloration to the flame.

The flame coloration shows a *blue centre* after the loop has been moistened with HCl, or if $CuCl_2$-solution was originally used.

Cadmium (Cd).

Density 8·6, melting point 320·9° C.

164. Cadmium is a white metal, and is fairly malleable and ductile. It is slightly attacked by moist air; and when it is strongly heated, it burns to the brown oxide, CdO.

The metal is readily soluble in the common acids. It forms one series of salts corresponding to the brown oxide, CdO. The Cd-ion is divalent and colourless.

Cadmium occurs in nature as greenockite, CdS, and is usually present in small quantity in zinc blende.

REACTIONS OF CADMIUM.

Use Cadmium sulphate, $3CdSO_4.8H_2O$.

165. **H_2S:** bright yellow precipitate (CdS). Boil off the H_2S and pour the liquid containing the precipitate into five tubes.

Show with these separate portions that the precipitate is insoluble in Am_2S, in KOH and in KCN-solution, but is soluble in boiling dilute HNO_3 and in boiling dilute H_2SO_4.

Dilute the H_2SO_4-solution of the precipitate with much water and pass H_2S for a short time; yellow CdS will be reprecipitated.

166. **AmOH,** if it is added in a very dilute condition and in small quantity, gives a white precipitate, $Cd(OH)_2$; when more AmOH is added, the precipitate will be readily dissolved.

167. **KOH:** white precipitate of $Cd(OH)_2$, insoluble in excess of KOH.

168. **KCN:** white precipitate of cadmium cyanide, $CdCy_2$, readily soluble in excess as the double cyanide K_2CdCy_4. From this solution H_2S reprecipitates CdS. (Difference from copper.)

169. **Blowpipe-test on Charcoal.**—If powdered $CdSO_4$ is mixed with Na_2CO_3 in a cavity on charcoal, and the mixture is then heated in the inner blowpipe-flame, a brown incrustation will be seen on the surface of the charcoal around the cavity.

DETECTION OF THE METALS IN GROUP II.A., WHEN THEY OCCUR TOGETHER.

170. **The following Differences** are utilised:—

1. The solubility of Bi_2S_3, CuS, and CdS in strong boiling HNO_3, in which HgS and PbS are insoluble and remain as HgS and $PbSO_4$ respectively after the treatment with the acid.

2. The solubility of $PbSO_4$ in a mixture of $H\bar{A}$ with excess of AmOH, or in $Am\bar{A}$-solution, HgS being insoluble in $Am\bar{A}$.

3. The solubility of $Cu(OH)_2$ and $Cd(OH)_2$, and the insolubility of $Bi(OH)_3$ in excess of AmOH.

4. The solubility of CdS, and the insolubility of CuS in boiling dilute H_2SO_4; or the formation of the double soluble cyanides of these metals with KCN, and the subsequent precipitation of the Cd as CdS by means of H_2S, the copper remaining in solution.

171. **A Solution which may contain the Metals of Group II.A.** is first made acid, if it is not already so, by adding to it HCl. Whether the liquid is clear or not, H_2S is then passed through it for about five minutes, and the precipitated sulphides are filtered off.

The clear filtrate is either mixed with H_2S-water, or it is diluted with a little water and H_2S is passed through it again for a short time, in order to ascertain whether the metals have been completely precipitated from the original solution.

If no further precipitate is produced, the filtrate may be rejected. But in case H_2S causes further precipitation, the gas is passed for some time longer and the liquid is then poured again through the filter. The filtrate is rejected only when H_2S no longer produces any precipitate in it.

The precipitate is then examined by Table II. (1252), commencing at Group II.A. Copper Group (1253), and using only the left-hand side of the Table.

GROUP II.B.—ARSENIC GROUP.

172. This Group includes As, Sb, Sn.

These metals differ from the metals of Groups III.A., III.B., IV., and V., by being precipitated as sulphides by H_2S from a solution which has been acidified with HCl. They differ from metals of Group I. by not being precipitated by HCl.

The sulphides of the metals of this Group differ from those of the metals in Group II.A. by being soluble in Am_2S and in KOH.

Each metal of this Group forms two series of compounds. These compounds resemble each other in many reactions, but they show distinctive differences in certain reactions. The two classes are conveniently distinguished by the terminations *-ous* and *-ic*, as in the two classes of mercury and copper salts; thus we speak of arsen*ious* oxide and arsen*ic* oxide, and of stann*ous* and stann*ic* chloride.

The Reactions of the Rarer Elements of this Group, Au, Pt, Ir, Mo, Se, Te, are given in paragraphs 220–261.

Arsenic (As).

The density is 4·7 in the amorphous state, and to 5·7 when crystalline. Arsenic sublimes without melting at a dull red heat, but it may be fused if it is heated under pressure.

173. Arsenic is a steel-grey metallic-looking substance; in moist air its surface becomes gradually covered with a film of oxide. When arsenic is heated it is converted into yellow vapour, which smells like garlic, and burns with a bright flame emitting white smoke (As_4O_6). Dilute acids have little action on this element, but concentrated acids attack it readily.

The arsen*ious* compounds correspond to the oxide As_4O_6, which is amphoteric in character, yielding with strong acids feeble salts such as $AsCl_3$, and with strong bases arsenites such as Na_3AsO_3.

Arsen*ic* compounds are converted into arsen*ious* by boiling them with H_2SO_3, with strong HCl, or with some other suitable reducing agent. Arsen*ious* compounds are oxidised into arsen*ic* compounds when they are heated with HNO_3, or with some other suitable oxidising agent.

For minerals containing As refer to par. 1419.

REACTIONS OF ARSENIC.

Use for an arsen*ious* compound, arsenious oxide (As_4O_6) dissolved in boiling water; and for an arsen*ic* compound, sodium hydrogen arsenate ($Na_2HAsO_4.12H_2O$) dissolved in water.

Many of the tests described in the following paragraphs give the same ultimate results with both arsen*ious* and arsen*ic* compounds; the reaction, however, usually proceeds more slowly with an arsen*ic* compound, since the first stage consists in its conversion into an arsen*ious* compound.

174. **H_2S** produces only a yellow coloration in neutral solution of an *arsenious compound.* But if the solution is acidified with a few drops of HCl, a light yellow flocculent precipitate (As_2S_3) will form immediately even in the cold.

Filter off some of the As_2S_3, and show that it is insoluble in boiling strong HCl.

Pour some of the liquid containing the precipitate into two test-tubes, and add KOH and Am_2S respectively drop by drop; each of these solutions will completely dissolve the As_2S_3 as arsenite and sulpharsenite respectively:—

$$As_2S_3 + 6KOH = K_3AsO_3 + K_3AsS_3 + 3H_2O.$$
$$As_2S_3 + 3Am_2S = 2Am_3AsS_3.$$

The As_2S_3 may be reprecipitated from these solutions by the addition of HCl in excess:—

$$K_3AsO_3 + K_3AsS_3 + 6HCl = As_2S_3 + 6KCl + 3H_2O$$
$$2Am_3AsS_3 + 6HCl = As_2S_3 + 6AmCl + 3H_2S.$$

Note.—Since the ammonium sulphide solution used as a reagent is commonly *yellow* and contains a polysulphide, and the reagent has been added in excess, the As_2S_3 when reprecipitated by HCl will usually be mixed with sulphur: $Am_2S_n + 2HCl = 2AmCl + H_2S + S_{n-1}$.

In cold acidified solutions of *arsenic compounds* H_2S produces no precipitate. But if strong HCl is added and the solution is boiled, H_2S will precipitate first white S and then yellow As_2S_3, when it is passed for some time into the boiling liquid.

The complete precipitation of arsen*ic* solutions by H_2S is most rapidly secured after they have been converted into the arsen*ious* state. This may be effected by boiling with strong HCl as above, or more rapidly by adding H_2SO_3 to the boiling arsen*ic* solution until it smells persistently of SO_2, and then boiling the liquid until SO_2 is no longer smelt. The arsenious compound thus produced may then be readily and completely precipitated by H_2S in the cold solution.

175. **Reinsch's test.**—Several narrow strips of sheet copper are cleansed, if necessary, by means of emery-paper, or by dipping them into strong HNO_3. They are then boiled in the arsenious solution, which has been previously acidified by dilute HCl. The surface of the copper will soon be coated with a dark grey film of copper arsenide.

The strips are carefully removed from the liquid, rinsed, and gently pressed between filter-paper ; they are then dried by heating them in the steam-oven, or by holding them in the fingers and heating them gently over the flame.

The dry strips are now gradually heated over a very small flame in a warm and dry test-tube. A white sublimate of As_4O_6 will form on the upper part of the tube.

A much more characteristic sublimate will be obtained, if moisture is entirely removed from the copper strips and from the tube, and if the sublimation is then effected very slowly and while the sides of the tube are hot.

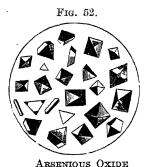



FIG. 52.

ARSENIOUS OXIDE CRYSTALS.

This sublimate will be sparkling and crystalline ; and if the crystals are examined under the microscope, they will be seen to be transparent, colourless, regular octahedra and tetrahedra (Fig. 52). The formation of these crystals under the above conditions is a most valuable confirmation of the presence of As.

The sublimate of As_4O_6 may be dissolved in a little boiling water, and the presence of As confirmed by applying tests 174 and 184 to separate parts of this solution.

The presence of As in the original grey deposit upon the Cu should always be confirmed by one of the above methods, since other metals may be deposited as grey films on Cu.

Reinsch's test will serve for the detection of arsenic compounds, after their solutions have been reduced to arsenious compounds by being mixed with strong HCl or with H_2SO_3-solution and boiled.

TESTS WHICH DEPEND UPON THE FORMATION OF ARSENIC HYDRIDE (AsH_3).

The following tests (176–180), which depend upon the formation of very poisonous gaseous AsH_3, should be performed in a closet provided with a good draught : this precaution is necessary in order to guard against any of the gas being inhaled.

176. Hofmann's test.—Pour dilute HCl upon some pure Zn in a small hydrogen-flask, fitted as is shown in Fig. 53.

The hydrogen may be washed, as it escapes, by letting it bubble through some water contained in the second flask, but this is not necessary.

Allow the hydrogen to pass through some $AgNO_3$-solution contained in a test-tube. If the Zn and acid are free from As, as they should be, no precipitate or colour will be produced in the $AgNO_3$-solution.

FIG. 53.

HOFMANN'S ARSENIC APPARATUS.

Now pour a few drops only of As_4O_6-solution down the funnel into the hydrogen flask; a black precipitate of Ag will soon form in the $AgNO_3$-solution, and H_3AsO_3 will remain dissolved.

This precipitate is produced by the AsH_3, which is formed by the action of the nascent hydrogen upon the As_4O_6:—

$$As_4O_6 + 12H_2 = 4AsH_3 + 6H_2O.$$

The AsH_3, on passing into the $AgNO_3$-solution, reacts thus :—

$$AsH_3 + 6AgNO_3 + 3H_2O = 3Ag_2 + H_3AsO_3 + 6HNO_3.$$

As soon as a copious precipitate has been obtained, the test-tube is removed.

It will be best to set aside the test-tube with its contents to be examined afterwards, and to proceed at once to use the gas, while it is being briskly evolved, for reactions 177 and 178.

The liquid in the test-tube is filtered; the precipitate is rejected, and several drops of $AgNO_3$-solution are added to the clear filtrate. Some very dilute solution of ammonia is made by pouring several drops of AmOH-solution into a test-tube, then nearly filling up with distilled water and inverting the tube. When this solution is mixed drop by drop with the filtrate, a light yellow precipitate of silver arsenite will be obtained.

In order to explain the formation of this precipitate, it must be remembered that the solution contains H_3AsO_3 in the presence of $AgNO_3$ and of HNO_3; and further that $AgNO_3$ forms a yellow precipitate with H_3AsO_3 if no free acid is present in the liquid (184). The formation of this precipitate is prevented by the HNO_3; but when sufficient AmOH is added to neutralise the free HNO_3 which is already present, as well as that which is formed by the action of $AgNO_3$ on H_3AsO_3, the yellow precipitate will appear :—

$$H_3AsO_3 + 3AgNO_3 + 3AmOH = Ag_3AsO_3 + 3AmNO_3 + 3H_2O.$$

This precipitate (Ag_3AsO_3) is, however, readily soluble in AmOH; hence it is necessary to use very dilute AmOH and to add it gradually in order to avoid excess, since if excess of AmOH is added the precipitate will be prevented from forming.

177. **Marsh's test.**—Disconnect the flasks (Fig. 53, p. 81), and slip into the rubber joint a tube of glass about four inches (10 cm.) in length, supporting it on the ring of a retort-stand (Fig. 54). Then pour in a little strong HCl through the funnel-tube.

Caution.—If the experiment is performed as is here directed, the hydrogen will have been already evolved for some time for the previous test (176), and will have expelled all the air from the flask. There will therefore be no risk of an explosion occurring when the gas is lighted, owing to mixture of air with the hydrogen.

But if the hydrogen is being produced for the first time, or if the flask has been opened or recharged, allow the gas to escape briskly for four or five minutes; and then ascertain that a test-tube, filled with the gas, burns quietly, before proceeding to kindle the gas at the jet. In any case it is well to cover the flask with a cloth before the hydrogen is kindled, in order to guard against any risks from an explosion.

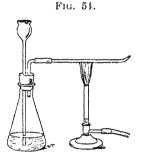



FIG. 54.

MARSH'S ARSENIC MIRROR.

Now light the hydrogen as it escapes from the jet (Fig. 54). The flame will be seen to differ from that of pure H by its livid blue colour, and by its evolution of white fumes of As_4O_6. If these appearances are not noticed, there is not sufficient arsenic solution in the flask: a few more drops of the arsenic solution must, therefore, be poured in through the funnel-tube.

Press down upon the flame the inside of a porcelain crucible-lid or of a porcelain crucible or dish. A dusky black film of As will be deposited upon the cool surface. Two porcelain surfaces should be thus stained with As.

Pour upon one of these stains some freshly-made solution of bleaching-powder; the stain will be rapidly dissolved.

Warm the second stain of As with yellow Am_2S. It will dissolve, and the solution will leave *yellow* As_2S_3 when it is slowly evaporated.

178. **Decomposition of AsH_3 by Heat.**—While the flame is still burning at the jet, pour a little more strong HCl into the flask (Fig. 54), if necessary, in order to produce a fair-sized flame. Then heat a point near the middle of the tube strongly (Fig. 54). A

black mirror of As will form just beyond the part which is heated by the flame. The flame burning at the jet will meanwhile become colourless, showing that the arsenic has been removed from the hydrogen.

Heat another point in the tube, so as to produce a second mirror; then remove the tube and divide it between the mirrors and confirm the presence of As as follows:—

Dissolve one mirror, when it is cold, by warming it in a test-tube with some freshly-made solution of bleaching-powder.

Heat the other mirror gently in a test-tube held obliquely in the flame; if the sides of the tube have been first heated, a crystalline sublimate of As_4O_6 will be obtained (Fig. 52, page 80). Dissolve this sublimate, when it is cold, in a little hot water and confirm the presence of As by trying reactions 174 and 184 on the solution.

179. **$HgCl_2$-solution** is coloured by contact with AsH_3.

Remove the cork from the generating flask (Fig. 53 or 54), and push a plug of cotton-wool into its neck in order to arrest any liquid spirted from the flask. Then cover the mouth of the flask with a small piece of filter-paper, which has been moistened with $HgCl_2$-solution; the paper will become coloured, first *yellow* and then *brown*. This result is distinctive from SbH_3, which gives only a greyish-brown stain.

If paper moistened with $AgNO_3$-solution is substituted for the above paper, it will be *blackened* (176): this is also the case with SbH_3.

180. **Fleitmann's test.**—Boil some pieces of Zn in KOH-solution: H will be slowly evolved, and will be free from odour. If a little As_4O_6-solution is now added and the liquid is again boiled, a garlic odour will be perceptible; the odour is due to the evolution of AsH_3:—

$$\begin{cases} Zn + 2KOH = H_2 + Zn(OK)_2. \\ As_4O_6 + 12H_2 = 4AsH_3 + 6H_2O. \end{cases}$$

If a small piece of filter-paper, which has been moistened with $AgNO_3$-solution, is placed on the mouth of the tube while the liquid is being boiled, the paper will be stained black by the separation of Ag (176).*

An arsenic compound must be reduced, by being boiled with H_2SO_3, before the above test is applied.

* Sb-compounds do not give the above result; the test therefore serves to distinguish between As and Sb.

REACTIONS OF SOLID ARSENIC COMPOUNDS.

181. Mirror of As by Reduction.—Dry some finely-powdered substance, containing As, thoroughly in the steam oven, and mix it intimately in a mortar with about four times its measure of freshly ignited Na_2CO_3, or of a perfectly dried mixture of KCN and Na_2CO_3. Heat this mixture in a little bulb-tube of hard glass (Fig. 55), or in a narrow test-tube about three inches (8 cm.) in length, carefully observing the precautions mentioned in paragraph 140. A black mirror of As will form on the cooler part of the tube (B), and a smell of garlic may usually be detected at the mouth of the tube.

FIG. 55.

ARSENIC MIRROR FROM SOLID ARSENIC COMPOUND.

If the bulb is cut off and the mirror is gently heated in a test-tube, the As will be converted into a white sublimate of As_4O_6, or into transparent octahedral crystals of the oxide (Fig. 52, page 80).

182. Blowpipe-reaction on Charcoal.—Mix a solid substance, containing As, with Na_2CO_3 and KCN, and heat the mixture on charcoal in the inner blowpipe-flame. The flame will be seen to be coloured *livid blue*, unless this tint is overpowered by the yellow sodium coloration. A smell of garlic will be noticed when the charcoal is removed from the flame.

183. Heat a little Solid As_4O_6 in a small ignition-tube: it will be readily sublimed. If the As_4O_6 is perfectly dry, and it is sublimed very slowly after the upper part of the tube has been first heated in the flame, the sublimate will sparkle, and when it is examined under the microscope, it will be seen to consist of octahedral crystals (Fig. 52, page 80).

DISTINCTIVE TESTS FOR ARSEN*IOUS* AND ARSEN*IC* COMPOUNDS.

Use As_4O_6 dissolved in boiling water for the arsen*ious* solution, and aqueous solution of sodium arsenate for the arsen*ic* compound.

184. $AgNO_3$: if several drops are added to the arsenious acid solution, and very dilute AmOH-solution is then added drop by drop, a *light yellow* precipitate of silver arsenite (Ag_3AsO_3) will form, which is soluble in AmOH and in HNO_3.

With arsenate, a *brown* precipitate of silver arsenate (Ag_3AsO_4) is produced, which is also soluble in AmOH and in HNO_3.

185. **$CuSO_4$**, if it is added to the arsenious solution, followed by a gradually increasing quantity of KOH-solution, yields first a *yellowish-green* precipitate, which then dissolves to a clear *blue* liquid: this liquid, when it is boiled, deposits *orange-red* Cu_2O.

With arsenate, the pale green precipitate forms, but it is not soluble in excess of KOH-solution, and it does not deposit Cu_2O when it is boiled.

186. **AmCl, AmOH and $MgSO_4$**: these solutions, added in the order stated, give no precipitate in the arsenious solution.

When they are added to the arsenate solution, a white crystalline precipitate of $MgNH_4AsO_4 . 6H_2O$ is produced, and if this is filtered off, and moistened on the filter with $AgNO_3$-solution, it turns brown (184).

Antimony (Sb).

Density 6·62, melting-point 630° C.

187. Antimony is a brittle, white, lustrous metal. It slowly tarnishes in moist air, and when it is fused and heated in the air it burns to Sb_4O_6.

Dilute acids scarcely act upon this metal, but concentrated hydrochloric and sulphuric acid convert it respectively into the trichloride and into an unstable sulphate. Hot strong nitric acid converts the metal into the insoluble oxides, Sb_2O_4 and Sb_2O_5.

The antimon*ious* compounds, corresponding to the oxide Sb_4O_6 are the important compounds of antimony. This oxide is feebly basic in character.

The antimonic compounds, corresponding to the oxide Sb_2O_5, are of little importance to the analyst.

For minerals containing Sb refer to par. 1419.

REACTIONS OF ANTIMONY.

Use Antimony trichloride ($SbCl_3$) solution, produced by dissolving $SbCl_3$ or Sb_4O_6 in dilute HCl.

Antimon*ic* and antimon*ious* compounds give results, which are ultimately identical, in the following reactions (188–195), with the exception of reaction 189. After these reactions, which are common to Sb in both its sets of compounds, two are given which are distinctive of the two classes of compounds (196, 197).

188. **H_2S**: orange-red precipitate (Sb_2S_3). Pour off the liquid with the precipitate into three tubes, and show that the precipitate

is dissolved when it is warmed with pure KOH or with Am_2S, but is reprecipitated from these solutions when HCl is added in excess (174 and *Note*). Show also that the precipitate is soluble in boiling strong HCl.

189. **H_2O.**—When $SbCl_3$-solution is poured into much water, it yields a white precipitate or turbidity (SbOCl): this basic salt is converted into the trioxide when water is added in large amount.

The precipitate is dissolved when HCl is added to the liquid and it is heated; it is also readily soluble in $H_2\bar{T}$. The solubility of SbOCl in $H_2\bar{T}$ distinguishes it from the similarly formed BiOCl precipitate (146).

190. **Zn and Pt.**—If the acid solution of $SbCl_3$ is poured upon some platinum-foil in a porcelain dish, and a small piece of Zn is dropped upon the foil, the platinum will be rapidly coated with a black deposit of Sb. If the foil is then rinsed with water and heated in boiling HCl, the stain will remain undissolved; but it will be rapidly removed by heating the foil with HNO_3.

The formation of a slight grey or brown stain on the Pt is no evidence of the presence of Sb. The presence of Sb in the stain may be proved by dissolving it in a little boiling dilute HNO_3, diluting the cold solution, and then passing H_2S and allowing it to stand at rest for some time, when red Sb_2S_3 will settle down.

TESTS WHICH DEPEND UPON THE FORMATION OF ANTIMONY HYDRIDE.

SbH_3 may be generated by pouring Sb-solution into a hydrogen-apparatus, as is directed in paragraphs 176–179, for an arsenic solution. Antimony hydride, SbH_3, is evolved. This gas differs from AsH_3 by being free from smell and from poisonous properties, and also in the respects mentioned in paragraphs 191–193.

The first test in paragraph 179 is also distinctive.

191. **If SbH_3 is passed into $AgNO_3$-solution** (176), it produces a black precipitate of $SbAg_3$:—

$$SbH_3 + 3AgNO_3 = SbAg_3 + 3HNO_3.$$

Filter off this precipitate, and reject the filtrate which will contain no Sb.

Wash the precipitate of $SbAg_3$ four or five times with boiling water upon the filter. Then pour upon it boiling dilute $H_2\bar{T}$-solution, which will dissolve the Sb. Receive this liquid in a test-tube, boil it, and pour it once more upon the filter. Now add HCl to the liquid, filter if necessary from AgCl, and pass H_2S into the acid solution; orange-red Sb_2S_3 will be precipitated.

192. A Stain of Sb on Porcelain, which has been produced in the manner already described in paragraph 177, differs from the As-stain by presenting a dead surface and by being insoluble in solution of bleaching-powder. Also when the stain is dissolved by warming it with yellow Am_2S, and the solution is evaporated by a gentle heat, a residue of *orange-red* Sb_2S_3 is left.

193. The Sb-mirror, obtained as is described in paragraph 178, differs from the As-mirror by being formed much nearer to the flame and on both sides of the heated part of the tube, proving that Sb is less volatile than As. The mirror may further be distinguished by the test which is described in paragraph 191.

The sublimate of Sb_4O_6, which is produced by heating this mirror in the air, differs from the corresponding arsenic sublimate (178) by being almost non-crystalline and insoluble in boiling water. The sublimate may, however, be dissolved in a little boiling HCl, and this acid solution yields an *orange-red* precipitate of Sb_2S_3 when H_2S is passed into it; whereas the solution of the As_4O_6 sublimate yields *yellow* As_2S_3 under similar conditions.

194, **Zn and KOH.**—If a solution containing Sb is boiled with Zn and KOH, it does not evolve SbH_3; hence the escaping hydrogen does not stain paper moistened with $AgNO_3$-solution (180). This test serves to distinguish As from Sb in its compounds.

TESTS FOR SOLID COMPOUNDS OF SB.

195. Blowpipe-test on Charcoal.—Mix a little solid substance containing Sb in a cavity on wood-charcoal with Na_2CO_3 and KCN, and heat the mixture in the inner blowpipe-flame.

A white incrustation will be formed on the charcoal; and white globules of metallic Sb will be obtained, which are extremely brittle (106). The flame will also be seen to be coloured pale blue, unless this tint is concealed by the yellow sodium coloration.

When the melted Sb-globules are withdrawn from the flame, they will emit white fumes and become coated with sharp white crystals of Sb_4O_6.

DISTINCTIVE TESTS FOR ANTIMON*IOUS* AND ANTIMON*IC* COMPOUNDS.

Use $SbCl_3$-solution in HCl, and aqueous potassium antimonate solution respectively.

196. KHO in excess, then $AgNO_3$: with $SbCl_3$, a dark coloured precipitate, which when shaken after addition of AmOH leaves black Ag_4O undissolved: with antimonate, a brown precipitate which dissolves entirely on addition of AmOH.

197. HCl in excess, warm, and KI-solution: with $SbCl_3$ no iodine is set free, the liquid remaining colourless, even after it has been mixed with fresh starch solution: with antimonate, iodine is liberated which colours the liquid brown, and gives a deep blue colour when starch solution is mixed with the cold liquid.

Tin (Sn).

Density varies from 6·6 to 7·3, melting-point 231·9° C.

198. Tin is a white, lustrous metal, and is both malleable and ductile. At ordinary temperature air has practically no effect upon it, but when the metal is heated above its melting-point in the air it gradually changes into the white dioxide, SnO_2.

Dilute hydrochloric or sulphuric acid slowly dissolves tin with formation of a stannous salt: the hot concentrated acids act more rapidly. Dilute nitric acid forms unstable stannous nitrate, and the concentrated acid forms white hydrated SnO_2.

Tin forms two series of compounds, the stann*ous* and stann*ic*, in which the metal is divalent and tetravalent respectively, and which correspond to the oxides SnO and SnO_2. Both oxides possess feeble basic and acidic properties.

For minerals containing Sn refer to par. 1419.

REACTIONS OF TIN.

Stannous and Stannic compounds.

Use for Stannous salt, $SnCl_2.2H_2O$ dissolved in dilute HCl, and for Stannic salt, $SnCl_4$ dissolved in dilute HCl.

The reactions 199 and 200 give ultimately the same results with both stann*ous* and stann*ic* compounds. Reactions 201, 202, and 203 serve to distinguish stannous from stannic salts, and to detect stannous salts in the presence of stannic salts.

199. Zinc, when it is immersed in the solution of a tin-salt which has been acidified with HCl, becomes coated with either a spongy mass or beautiful crystals of Sn.

The Zn should be allowed to remain for some time in the solution, which is contained in a small porcelain dish, and the reaction may be hastened by the application of a gentle heat. The deposition of Sn from $SnCl_2$ takes place more rapidly than from $SnCl_4$, since $SnCl_4$ has to be first converted into $SnCl_2$.

If the Zn rests upon platinum-foil in the solution, the Sn will be deposited in a spongy state on the Zn and will not stain the platinum black. Sn differs in this way from Sb (190).

In general analysis the deposit on the Zn may consist of other substances besides Sn. It should, therefore, be removed by rubbing

and washing the Zn in some water in the porcelain dish; the deposit may then be rinsed into a narrow test-tube, and dissolved in a little boiling strong HCl. This solution will contain $SnCl_2$, which will yield with $HgCl_2$-solution a white precipitate of Hg_2Cl_2 (135, 202).

Since this precipitation of Hg_2Cl_2 depends upon the formation of $SnCl_2$ and its presence in the acid solution, and since $SnCl_2$ is readily converted into $SnCl_4$ by oxidation in the acid liquid, precautions must be taken against exposing the acid solution freely to the air. It will usually suffice to dissolve the deposit quickly in a narrow test-tube, and to proceed at once to add the $HgCl_2$-solution.

200. **Blowpipe-test on Charcoal.**—Mix any solid compound, containing Sn, with powdered Na_2CO_3 and KCN, and heat the mixture on charcoal in the inner blowpipe-flame. A slight white incrustation will be obtained, together with white particles of metallic Sn which are with difficulty fused into globules.

The globules of Sn are malleable; they differ from those of Pb by their greater hardness, which prevents them from marking paper. Refer to paragraph 106 for a description of the methods of testing these globules.

DISTINCTIVE REACTIONS FOR STANN*OUS* AND STANN*IC* COMPOUNDS.

201. **H_2S**: *dark brown* precipitate (SnS) with stannous solution, soluble in boiling strong HCl, also soluble in KOH and when warmed with yellow Am_2S, and reprecipitated as brown SnS from the KOH-solution by HCl, and as yellow SnS_2 from the Am_2S-solution (*Note*, 174). SnS is insoluble in colourless Am_2S.

With stannic solution, a *yellow* precipitate (SnS_2) which often forms only when the liquid is heated: soluble both in yellow and in colourless Am_2S and in KOH when heated, and reprecipitated as SnS_2 by HCl from both solutions (*Note*, 174).

202. **$HgCl_2$**: white precipitate of Hg_2Cl_2 with stannous solution, which turns grey when the liquid is boiled if the $SnCl_2$ is present in excess (135).

No precipitate is produced with stannic solution.

203. **$AuCl_3$** added after a drop of Br-water: with stannous solution a *purple* or *dark brown* precipitate of "purple of Cassius."

No precipitate is produced with stannic solution.

DETECTION OF METALS IN GROUP II.B., WHEN THEY OCCUR TOGETHER.

Three methods for the separation and detection of As, Sb and Sn are given. The first, which is described in paragraph 205, is simple and can be rapidly

carried out, but the methods of Hofmann (206) and Fresenius (207) are more delicate and trustworthy.

204. The following Differences are utilised in the first method :—

1. The solubility of Sb_2S_3, SnS and SnS_2 in hot strong HCl, in which As_2S_3 is insoluble.

2. The action of Zn and Pt in the presence of HCl upon the solution, Sb staining the platinum, and Sn being deposited upon the Zn (190, 199) : or the treatment of the HCl-solution with Zn, when the Sn is deposited on the Zn (199), and the Sb is evolved as SbH_3 gas (191–193).

FIRST METHOD.

205. From a Solution which may contain As, Sb, and Sn, these metals are first precipitated as sulphides by passing H_2S into the acidified solution. The sulphides are then filtered off, and the filtrate is tested by passing H_2S through it again and warming to prove that the precipitation has been complete, this procedure being repeated if necessary. When no further precipitate is produced by H_2S the precipitated sulphides are examined in the following manner, based on the above differences (204).

The precipitate produced by H_2S is filtered off, and is then allowed to drain for some time upon the filter in the funnel.

It is best to drain the precipitate still further, either by suction of the filter-pump (44), or by opening out the filter and spreading it upon a pile of three or four cut filter-papers.

The precipitate is then removed to a small porcelain dish, and is heated for some time, nearly to boiling, with strong fuming HCl. The liquid is then cooled and filtered :—

The Residue will consist chiefly of As_2S_3, which is almost insoluble in strong HCl. It may be examined by either I or II below :—

I. Dry the washed residue on the filter at a gentle heat, then mix it with three or four times as much powdered

The Filtrate may be examined for Sb and Sn by either I. or II. below :—

I. Place a piece of platinum-foil in a porcelain dish and pour the acid filtrate upon it, then place upon the foil a piece of Zn ; H will come off with effervescence, and if either at once or after a few minutes a black stain appears upon the platinum this shows :—**Presence of Sb.**

[The Sb thus deposited on the Pt may be rinsed and then dissolved by heating the foil in a test-tube with a little very dilute HNO_3 ; if this solution is cooled and diluted, and H_2S is passed through it, an orange-red precipitate will be formed, confirming the presence of Sb.]

KCN and Na_2CO_3, and heat the mixture in a small bulb-tube, removing any drops of water inside the tube by a twisted piece of filter-paper; a black mirror (181):— **Presence of As.**

II. Or the As_2S_3 may be dissolved by heating it with a little fuming HNO_3. The excess of HNO_3 is then boiled off and the As is detected as H_3AsO_4 by adding AmCl, excess of AmOH and $MgSO_4$ (186); or by adding $AgNO_3$ and then cautiously neutralising with AmOH (184).

Remove the platinum-foil from the dish and place pieces of Zn in the acid liquid; as soon as the bubbles of H cease to be given off, Zn still remaining undissolved, remove the pieces of Zn, rubbing and rinsing any dark deposit back into the dish: let this deposit settle, decant the liquid, and heat the solid deposit with strong HCl for several minutes in a test-tube, dilute with a little water, filter if necessary, and add a few drops of $HgCl_2$-solution; a white or grey precipitate (135, 202) indicates:—**Presence of Sn.** The original solution may then be examined to find whether the Sn was present as stannous or stannic salt (201–203.)

II. The acid filtrate is poured into a little hydrogen flask (Fig. 54, p. 82), in which H has been coming off briskly for about five minutes, being produced by the action of a little strong HCl upon some pieces of pure Zn. The H is lighted at the jet, and the inside of a small porcelain dish or crucible lid is pressed down upon the flame; a black stain, which is not dissolved by solution of bleaching-powder, shows:—**Presence of Sb.**

The residue in the flask is tested for Sn, as is directed in the latter part of I. (above).

SECOND METHOD.

206. **Hofmann's method** depends upon the different results obtained by the action of Zn upon the dissolved chlorides of the metals in the presence of HCl. The Sn is deposited upon the Zn, and AsH_3 and SbH_3 gases are evolved. These gases are allowed to react upon silver nitrate solution, when the As passes into solution as H_3AsO_3 and the Sb is precipitated as $SbAg_3$.

The sulphides, which have been precipitated as is directed in paragraph 205, are warmed with a little strong HCl, and a small crystal of $KClO_3$ is occasionally dropped in until solution is complete. The warming of the liquid is then continued until no smell of Cl is evolved.

This solution of the metals is then poured into a suitable flask, in which H is being generated by the action of HCl upon pure Zn (Fig. 53, p. 81). Sn, Au and Pt, if present, will be deposited upon the Zn, while As and Sb will be evolved as gaseous AsH_3 and SbH_3. These two gases are passed into $AgNO_3$-solution, and yield H_3AsO_3 in solution and Ag_3Sb as a black precipitate.

The $AgNO_3$-solution, containing the black precipitate, is filtered:—

Precipitate: wash this well upon the filter, and pour upon it some boiling $H_2\bar{T}$-solution. Boil this liquid again and pour it several times on the filter. Now add HCl and pass H_2S: a red coloration or precipitate indicates:— **Presence of Sb.**

Filtrate: add to this some very dilute AmOH, drop by drop, with constant mixing by stirring or shaking; a pale yellow flocculent precipitate indicates:—**Presence of As.**

The Deposit of Sn is removed from the Zn in the flask, and is washed. It is then dissolved by boiling it with a little strong HCl in a narrow test-tube: any residue being examined by paragraph 1305, if Au and Pt have to be tested for. The solution in HCl is *at once* diluted and is tested for $SnCl_2$ by the addition of $HgCl_2$-solution: a white precipitate, possibly turning grey (135, 202), shows:—**Presence of Sn.**

A further test is made, if necessary, upon the original solution in order to ascertain whether the tin was present as stannous or as stannic salt (201–203).

THIRD METHOD.

207. **Fresenius' method depends upon the fact** that fusion with Na_2CO_3 and $NaNO_3$ converts As_2S_3 into soluble Na_2HAsO_4, Sb_2S_3 into insoluble $Na_2H_2Sb_2O_7$, and SnS and SnS_2 into insoluble Sn or SnO_2.

The Sulphides, which have been precipitated as is directed in paragraph 205, are dried on the filter, and the precipitate is well mixed with equal weights of powdered Na_2CO_3 and $NaNO_3$.

If the quantity of the precipitate is very small, the part of the paper which contains the precipitate is cut up into small pieces, and these are treated as is directed for the precipitate.

This mixture is dropped in small quantities at a time into some $NaNO_3$, which is fused in a small porcelain crucible over a Bunsen-flame. When the powder has all been added, the crucible is heated sufficiently to keep the mixture melted for a few minutes, and the liquid mass is then poured into a small dry porcelain dish.

As soon as the substance has cooled, cold water is poured upon it in the dish, and water is also poured upon the residue which adheres to the inside of the crucible. The solid substance is allowed to soak in the water in both vessels for some time with occasional stirring, crushing it by pressure with a pestle if it does not easily fall to pieces; the liquid is then filtered:—

The Residue is washed on the filter with a mixture of equal measures of water and alcohol, in which $Na_2H_2Sb_2O_7$ is insoluble; the washings are rejected.

The precipitate is then rinsed into a small porcelain dish, using as little water as possible; a few drops of strong HCl are added and the dish is heated, more HCl being added, if necessary, to make the liquid acid to litmus-paper.

Whether the residue has dissolved or not, place in the liquid a piece of clean platinum-foil, and drop upon the foil a piece of pure Zn. Remove the foil after a few seconds: a black stain shows: **Presence of Sb.** The presence of Sb may be confirmed by dissolving it off the foil with a little hot dilute HNO_3, cooling and passing H_2S, when a red precipitate of Sb_2S_3 will form.

When the Zn ceases to be acted upon, Sn if present will remain as a spongy deposit. This is to be washed by decantation, and then dissolved by boiling with HCl in a test-tube: $HgCl_2$ is added immediately to the solution: a white precipitate (202) shows:— **Presence of Sn.** The original solution is then tested, if necessary, to find whether Sn was present in the stannous or stannic condition.

Any residue insoluble in HCl should be examined for Au and Pt (1305).

Filtrate: HNO_3 is added until the solution is just acid after being boiled; then $AgNO_3$-solution is poured in as long as it causes any precipitate, and very dilute AmOH is added little by little (*Note*); a brown precipitate, readily dissolving in excess of AmOH (184), shows:—**Presence of As.**

Note. — Instead of mixing dilute AmOH with the liquid, AmOH may be carefully poured upon the top of the liquid; a brown colour is then seen at the surface of contact.

REACTIONS OF THE RARER ELEMENTS IN GROUP II.

208. The Rarer Elements of this Group are divided into two classes: those belonging to Group II.A. are Pd, Os, Rh, Ru; those belonging to Group II.B. are Au, Pt, Mo, Se, Te, Ir.

GROUP II.A.—COPPER GROUP.

209. In this Group are included Pd, Os (Rh, Ru); these metals are precipitated as sulphides by H_2S from acid solutions, and the sulphides are insoluble in Am_2S and in solution of alkaline hydroxide.

Palladium (Pd).—Use solution of Palladious chloride, $PdCl_2$.

210. Pd occurs as a metal in native platinum, also in gold and in silver: it has a density of 11·4. Palladious solutions are reddish-brown, and become yellow on dilution: the addition of water precipitates from these solutions a basic salt, unless sufficient free acid is present to prevent the precipitation.

Palladic compounds are also known, such as $PdCl_4$; they give the same reactions as palladious compounds, since they readily change into the palladious state.

211. H_2S: black precipitate in neutral, alkaline, and acid solutions; this precipitate is insoluble in Am_2S, but soluble in boiling HCl and in aqua regia.

212. AmOH: flesh-coloured precipitate Pd $(NH_3)_2''Cl_2$; soluble in excess of AmOH to a colourless liquid, from which HCl precipitates the isomeric yellow crystalline palladammonium chloride.

213. $HgCy_2$: yellowish-white gelatinous precipitate ($PdCy_2$), slightly soluble in HCl, easily soluble in AmOH and in KCN-solution. This is a very characteristic reaction.

214. KI: black precipitate (PdI_2); a very characteristic reaction.

215. Dry test: all Pd-compounds are decomposed by ignition, leaving the metal as a residue.

Osmium (Os).—Use solution of K_2OsCl_6. Density of the metal 22·48.

216. H_2S: brownish-black precipitate of OsS, insoluble in Am_2S.

217. KOH, AmOH or K_2CO_3: reddish-brown precipitate of $Os(OH)_4$.

218. Tannic acid or Alcohol, when it is added to the solution previously acidified with HCl, reduces the osmic chloride to blue osmious chloride, $OsCl_2$.

219. Formation of OsO_4: after acidifying a little of the solution with dilute HNO_3, distil it and receive the distillate in KOH-solution. The alkaline solution will be coloured yellow by the formation of potassium osmiate. Acidify this solution, and note the penetrating odour of the liberated OsO_4. Also add a little $Na_2S_2O_3$-solution to a portion of the distillate: when this is warmed a brown precipitate of osmium sulphide will be produced.

GROUP II.B.—ARSENIC GROUP.

220. In this Group are included Au, Pt, Mo, Se, Te, (Ir).

Gold (Au).—Use solution of Gold chloride.

221. Metallic gold is yellow; it has a density of 19·3, and melts at 1061°; it is the most ductile metal known. Gold is unaffected by air under all conditions. It is insoluble in all the common liquids and acids, but is dissolved by chlorine- or bromine-water, and by aqua regia. Two unstable, weakly basic oxides are known, Au_2O and Au_2O_3. The light yellow solution of gold in aqua regia contains both $AuCl_3$ and $HAuCl_4$, and is known as gold chloride solution: it is used for analytical and photographic purposes.

222. H_2S: in cold solutions black Au_2S_2 is precipitated, soluble in yellow Am_2S; in hot solutions brown metallic gold is precipitated.

223. $SnCl_2$ **containing a little** $SnCl_4$: purple or dark brown precipitate of "Purple of Cassius," which is best seen when the test is made in a white porcelain dish. This precipitate consists of very finely divided gold mixed with hydrated stannous oxide.

224. $FeSO_4$**-solution** produces, either at once, or when the solution is heated, a very finely-divided precipitate of Au. The particles of the precipitate cannot be seen, but they usually cause the liquid to appear bluish by transmitted light, and always copper-red and turbid by reflected light:—

$$AuCl_3 + 3FeSO_4 = Au + Fe_2(SO_4)_3 + FeCl_3.$$

225. H_2O_2: in alkaline solution gold is immediately precipitated in a finely-divided brownish-black condition: the liquid only appears reddish in colour if the gold is in very small quantity, and no precipitate is seen. This reaction is very delicate.

Platinum (Pt).—Use solution of Platinic chloride, or chlorplatinic acid, H_2PtCl_6.

226. Platinum has a density of 21·5, and melts at 1755° C. The metal is greyish-white in mass, but is known also as a black finely-divided powder "platinum black." Platinum is not acted on by air under any conditions but forms a brittle carbide when it is strongly heated in contact with soot or hydrocarbon gases. No ordinary acids affect it, but it is slowly acted on by chlorine- or bromine-water, and is readily dissolved by aqua regia, yielding a reddish-yellow solution which contains H_2PtCl_6, chlorplatinic acid. This solution is used for analytical purposes under the name of platinic chloride solution.

Platinum forms two unstable feebly basic oxides, PtO and PtO_2.

227. H_2S: black precipitate (PtS_2), which forms slowly in the cold, but more rapidly when the liquid is warmed. The precipitate is soluble in yellow Am_2S and in aqua regia.

228. **AmCl**, added to a strong solution, produces on standing for some time, or more quickly on being stirred, a yellow precipitate (Am_2PtCl_6), which is soluble in much hot water.

229. **KCl**: yellow crystalline precipitate of K_2PtCl_6: the addition of a little alcohol hastens the precipitation.

230. **Formic acid** precipitates from neutral boiling solutions all the platinum as a black powder: an acid solution must be previously neutralised by sodium hydroxide solution.

231. **$SnCl_2$** gives a reddish-brown colour (H_2PtCl_4) in the solution acidified with HCl:—$H_2PtCl_6 + SnCl_2 = H_2PtCl_4 + SnCl_4$.

The Method of Separating and Detecting Au and Pt is fully given in paragraph 1305.

Iridium (Ir).—Use solution of Na_2IrCl_6.

232. **H_2S:** the dark red colour of the solution is discharged, sulphur is deposited, and eventually a brown precipitate of Ir_2S_3 is deposited: the precipitate readily dissolves in Am_2S.

233. **KOH:** the colour of the cold solution changes to green; and when the solution is warmed its colour first changes to reddish, and finally to azure blue:—$2IrCl_4 + 2NaOH = 2IrCl_3 + NaCl + NaOCl + H_2O$.

234. **KCl:** brownish-black precipitate of K_2IrCl_6, insoluble in alcohol.

235. **Reducing reagents,** $SnCl_2$- or $FeSO_4$-solution, change the colour of the solution to green by reducing the $IrCl_4$ to trichloride; or they precipitate the metal as a black powder, as is the case with Zn.

Molybdate (MoO_4).—Use Am_2MoO_4-solution.

236. Mo occurs as molybdate: also as sulphide, which may be readily converted into MoO_3 by heating it in the air with HNO_3. Unignited MoO_3 dissolves in acids; ignited MoO_3 is insoluble in acids, but is easily soluble in alkali and in ammonium hydroxide solution.

237. **HCl, HNO_3, or H_2SO_4,** if it is added in small quantity to an aqueous solution of a molybdate, yields a white precipitate of H_2MoO_4 which is readily soluble in excess of the acid.

238. **H_2S,** added in very small quantity to the acidified solution, gives a blue liquid; if H_2S is added in larger quantity, a brown precipitate (MoS_3) forms; the precipitation becomes complete only when the solution is heated and H_2S is passed for some time. This precipitate is soluble in solution of alkaline sulphide or of alkaline hydroxide; MoS_3 is reprecipitated from this solution when acid is added in excess.

239. **Zn, or $SnCl_2$,** if it is added to the solution of a molybdate in HCl, colours it brown, green, or blue, according to its state of concentration

240. **KCNS,** if it is added to a solution acidified with HCl, gives no coloration; but if a piece of Zn is afterwards dropped into the liquid, a beautiful *crimson* colour is produced: when this liquid is shaken with ether, the colour is taken up by the ether.

241. **Na_2HPO_4,** if it is added in very small quantity to the solution of molybdate acidified with HNO_3, gives a yellow precipitate of ammonium phospho-molybdate when the liquid is gently warmed; this precipitate is readily soluble in excess of alkaline hydroxide solution.

242. **Borax-bead:** outer flame, *yellow*; inner flame, *dark brown*.

243. **Microcosmic-bead:** outer and inner flames, *green*.

Selenium (Se).—Use PbSe, K_2SeO_3, and K_2SeO_4.

244. Se occurs as selenide of Pb, Fe, Cu, Ag: also in small quantities in pyrites, and when this pyrites is burnt for the manufacture of sulphuric acid the Se is deposited in the leaden chambers. Selenium forms selenides, selenites and selenates, which are analogous to the corresponding sulphur compounds.

I. Selenide (Se.)—Use PbSe.

245. **When a Selenide is heated** in an open tube it evolves a smell of decaying horse-radish, and produces a grey or red sublimate of Se: the smell is very characteristic.

II. Selenite (SeO_3).—Use K_2SeO_3 (251).

246. **H_2S** gives in a cold acid solution a *yellow* precipitate, and in a hot acid solution a *reddish-yellow* precipitate:—$H_2SeO_3 + 2H_2S = Se + S_2 + 3H_2O$. This precipitate is soluble in Am_2S.

247. **$BaCl_2$** gives in a neutral solution a white precipitate ($BaSeO_3$): soluble in HCl and in HNO_3.

248. **$SnCl_2$ or H_2SO_3** gives in the presence of free HCl a *red*, or in warm solutions a *grey* precipitate of Se.

249. **Cu** in a hot solution acidified with HCl becomes covered with a black film, and the liquid, on standing with the Cu for some time, becomes coloured red by Se.

250. **$CuSO_4$:** green crystalline precipitate: selenates give no precipitate.

III. Selenate (SeO_4).—Use K_2SeO_4.

251. **HCl** produces no change in the cold; but when the liquid is boiled, Cl is given off and the selenate is reduced to selenite, to which the above tests (246–250) may be applied:—$K_2SeO_4 + 2HCl = K_2SeO_3 + Cl_2 + H_2O$.

252. **$BaCl_2$:** a white precipitate ($BaSeO_4$); insoluble in cold HCl; dissolved by boiling with HCl, with evolution of Cl:—$BaSeO_4 + 4HCl = H_2SeO_3 + BaCl_2 + Cl_2 + H_2O$. This behaviour with boiling HCl serves to distinguish and to separate the $BaSeO_4$ precipitate from the similar $BaSO_4$ precipitate.

IV. Selenium in any form of Combination.

253. **When it is heated on Charcoal in the Inner Blowpipe-flame** a solid selenium compound evolves a smell of rotten horse-radish.

254. **When it is heated on Charcoal with Na_2CO_3 in the Inner Blowpipe-flame** a selenium compound yields a fused mass, which when cooled and moistened on Ag yields a black stain Ag_2Se, and on addition of HCl evolves H_2Se, a badly smelling gas.

Tellurium (Te).—Use PbTe, K_2TeO_3, K_2TeO_4, as is directed below.

255. **Te** commonly occurs united with the metals Au, Ag, Bi, Cu, Fe.

Telluride (Te).—**Use Lead telluride, PbTe.**

256. **When a Telluride is heated in an open glass tube,** it gives white fumes and a sublimate; the sublimate differs from that given by Sb, by being fusible before the blowpipe.

II. Tellurite $(TeO_3)''$.—**Use** K_2TeO_3 (260).

257. H_2O **:** on dilution with water, tellurous acid is precipitated from the acid solution.

258. H_2S **:** in acid solutions a brown precipitate (TeS_2), easily soluble in Am_2S.

259. H_2SO_3**,** $SnCl_2$**, or Zn** precipitates black Te from a solution which is not strongly acid.

III. Tellurate $(TeO_4)''$.—**Use** K_2TeO_4.

260. **HCl** produces no change in the cold solution of a tellurate; but when the liquid is boiled, Cl is evolved and the tellurate is reduced to tellurite, the solution then gives the above reactions (257–259).

IV. Tellurium in any form of Combination.

261. **If it is fused with** Na_2CO_3 **on Charcoal in the Inner Blowpipe-flame,** a tellurium compound gives sodium telluride, a solution of which gives a black stain on Ag. When this solution is acidified it deposits black Te, and evolves H_2Te.

For the Detection of the Rarer Elements in Group II., see the second column in Table, paragraph 1323.

GROUP III.—IRON AND ZINC GROUPS.

262. The Group includes Al, Fe, Cr, Zn, Mn, Ni, Co, together with the rarer metals U, In, Be, Ti, V, Zr, Ce, Ta, Nb, La, Di, Yt, E, Th. It is conveniently subdivided into Groups III.A. and III.B. The reactions of the rarer metals of this group are given in paragraphs 326–397.

GROUP III.A.—IRON GROUP.

263. The Group includes Al, Fe, Cr.

The members of this Group are not precipitated by the group-reagents for Groups I and II and they differ from those of Groups III.B., IV., and V. by being precipitated from their solutions when AmOH is added in excess after AmCl. This Group is also precipitated by Am_2S, or by H_2S added in excess to the ammoniacal solution.

Group III.A. further differs from Group III.B. by being completely precipitated by adding $BaCO_3$ shaken up with water. This reagent affords the most perfect means of separating these two Sub-groups from one another, unless the metals are present in solution as sulphates when both groups are precipitated.

The members of Group III.A. show no characteristic flame-colorations; but, with the exception of Al, they impart a characteristic colour to the borax-bead.

Aluminium (Al).

Density 2·58, melting point 658·7° C.

264. Aluminium is a white, lustrous metal, and is very slightly acted upon by moist air; it is malleable and ductile, but not very tenacious.

The metal dissolves slowly in cold hydrochloric acid, but rapidly when heated: nitric acid has scarcely any action upon it. Cold sulphuric acid scarcely affects the metal, but the hot concentrated acid dissolves it. Alkaline hydroxide solutions rapidly dissolve the metal with evolution of hydrogen and formation of aluminates :—$Al_2 + 6KOH = 3H_2 + 2K_3AlO_3$.

Aluminium forms only one series of salts, and the trivalent ion is colourless and feebly basic.

For minerals containing Al refer to par. 1419.

Reactions of Aluminium.

Use Ammonium alum, $AlAm(SO_4)_2.12H_2O$.

265. AmOH : colourless flocculent precipitate, $Al(OH)_3$, which is often transparent and invisible until it has been coagulated by boiling the liquid: it is soluble in HCl and in $H\bar{A}$, and is slightly soluble in AmOH in the absence of AmCl.

266. KOH added in very small quantity: colourless flocculent precipitate, $Al(OH)_3$, soluble in excess of KOH :—

$$Al(OH)_3 + 3KOH = K_3AlO_3 + 3H_2O.$$

Add dilute HCl gradually to part of the KOH-solution of the precipitate until the liquid is neutral, the $Al(OH)_3$ will be reprecipitated. If more acid is added the precipitate will dissolve, but will reappear when AmOH is added in slight excess.

From another portion of the KOH-solution of the precipitate the $Al(OH)_3$ may be reprecipitated by the addition of sufficient AmCl-solution.

267. Ammonium sulphide, Am_2S : the same precipitate of $Al(OH)_3$, H_2S gas being evolved or remaining dissolved in the liquid :—

$$Al_2(SO_4)_3 + 3Am_2S + 6H_2O = 2Al(OH)_3 + 3Am_2SO_4 + 3H_2S.$$

268. **Blowpipe-test.**—Heat some solid alum on charcoal in the outer blowpipe-flame; then moisten it, after cooling, with $Co(NO_3)_2$-solution and again heat it in the outer flame; a *fine blue mass* will be obtained.

Iron (Fe).

Density 7·8, melting-point 1500° C.

269. Metallic iron readily oxidises or "rusts" in moist air, and is eventually converted into hydrated ferric oxide.

When the metal is heated strongly in air, or in oxygen, it is converted into the black oxide, Fe_3O_4.

Iron readily dissolves in acids: hydrochloric and sulphuric acids yield the corresponding ferrous salts, but nitric acid produces a ferric salt and evolves reddish-brown gases.

Commercial iron is never pure. It usually contains small quantities of carbon, sulphur, phosphorus, silicon and manganese, and frequently traces of other substances. When commercial iron is dissolved in HCl or in H_2SO_4 the hydrogen which escapes is accompanied by small quantities of gases, such as hydrocarbons, hydrogen sulphide, and hydrogen phosphide, and these impart to the gas an unpleasant odour. There is always a residue left after the action of the acid is complete, which consists mainly of carbon.

For minerals containing Fe refer to par. 1419.

270. Two classes of iron-compounds are known, corresponding to the oxides FeO and Fe_2O_3. They differ in appearance and properties and behave differently with reagents. They are known as *ferrous* and *ferric* compounds respectively. Ferric salts are usually yellow or reddish-yellow. Ferrous salts are usually pale green if they are in solution, or are combined with water (hydrated), and are white if they are perfectly free from water or "anhydrous."

The metal in ferrous compounds is divalent and is often distinctively termed *ferrosum*; in ferric compounds the metal is trivalent and may be termed *ferricum*.

271. It is usual to ascertain in which state of combination the iron exists, and some distinctive tests are therefore described below.

The whole of the reactions of ferrous compounds are not given, because Fe is always separated and detected in the course of analysis as a ferric compound, and ferrous compounds are subsequently tested for by trying special tests upon the original substance.

Ferrous compounds are readily converted into ferric compounds by heating them for a short time with an oxidising agent, such as a little strong HNO_3, or HCl and a crystal of $KClO_3$, or Br-water.

Both classes of compounds give the same results in the blowpipe-reactions (275, 276).

REACTIONS OF IRON.

Use $FeCl_3$ and $FeSO_4.7H_2O$.

272. **AmOH,** or **KOH :** with ferric salt the Fe is completely precipitated as a reddish-brown flocculent precipitate, $Fe(OH)_3$, which is insoluble in KOH, and soluble in HCl.

With ferrous salt the Fe is only partially precipitated as a dingy-green precipitate, which ultimately turns to brown $Fe(OH)_3$ on exposure to the air.

273. **Am_2S :** a black precipitate (FeS) is obtained with both ferrous and ferric salts, but it is mixed with white sulphur in the case of ferric salts :—

$$2FeCl_3 + 3Am_2S = 2FeS + S + 6AmCl.$$

FeS is soluble in boiling acids, but is insoluble in KOH.

In very dilute iron-solution a green colour only is produced at first by Am_2S, but black FeS separates after the liquid has stood for some time or when it is boiled.

274. **H_2S,** either passed as gas into the solution, or added as H_2S-water, gives a black precipitate (FeS) when the iron-solution is subsequently mixed with excess of alkaline hydroxide.

In neutral or acid solution of ferric salt, sulphur is precipitated and the ferric salt is converted into ferrous salt ; the colour of the solution therefore changes from yellow to pale green : this change of colour is visible in a strong solution, after it has been boiled and filtered :—$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S$.

275. **Heated with Solid Sodium carbonate (Na_2CO_3) and Potassium cyanide (KCN) on Charcoal** in the inner blowpipe-flame, a solid iron compound leaves a grey powder of metallic iron (60). This may be separated by levigation (61), and shown to be *magnetic* by being attracted when it is touched under water with the end of a magnet, or with the point of a magnetised knife-blade.

276. **A Borax-bead** containing Fe is *reddish-brown* while hot and *yellow* when cold, after it has been fused in the outer blowpipe-flame : after fusion in the inner-flame it is *olive-green*.

DISTINCTIVE TESTS FOR FERROUS AND FERRIC SALTS.

Use acidified solutions of $FeCl_3$ and $FeSO_4$.

277. **KOH or AmOH** gives distinctive precipitates (272).

278. **Potassium ferrocyanide, K_4FeCy_6 :** with ferric solution

dark blue precipitate, " prussian blue," insoluble in HCl and turned brown by KOH-solution.

With ferrous solution a *light blue* precipitate, which becomes dark blue by oxidation in the air or when it is treated with HNO_3 or Br-water.

279. **Potassium ferricyanide, K_3FeCy_6:** in freshly made solution (*Note*) darkens the colour of a ferric solution, but produces no precipitate, as is seen when the liquid is diluted.

With ferrous solution a dark blue precipitate, " Turnbull's blue," is produced. which is insoluble in HCl. A dark bluish-grey colour only is produced in very dilute ferrous solutions.

Note.—This solution must be made immediately before it is used, by dissolving a small piece of solid potassium ferricyanide, about the size of a pin's head, in a few drops of water.

280. **Potassium thiocyanate, KCNS:** with ferric solution a *blood-red coloration*, but no precipitate: the presence of HNO_3 or of $H\bar{A}$ hinders the reaction. The colour is immediately destroyed when a few drops of the red liquid are mixed with $HgCl_2$-solution.

With ferrous solution no coloration is produced by KCNS unless ferric salt is present in small quantity.

Chromium (Cr).

Density 6·92, melting-point 1505° C.

281. Metallic chromium is very hard and has the appearance of cast iron. When it is heated in the air to a high temperature it is converted into Cr_2O_3. The metal is readily soluble in hydrochloric acid and in sulphuric acid, but is practically insoluble in nitric acid.

There are two well-known series of chromium compounds: the chromic salts, which correspond to the basic oxide Cr_2O_3, and in which Cr is trivalent; and the chromates which contain the acidic oxide CrO_3.

The chromic salts, which are usually purple in colour, give the reactions which are described in paragraphs 282–287.

The chromates, which are usually yellow or reddish in colour, give the reactions which are described in paragraphs 639–644.

The chromium salts pass by oxidation into chromates in reactions 285 and 286, where the oxidation is caused by PbO_2 and by KNO_3 respectively.

Chromates, on the other hand, pass by reduction into green chromic compounds; examples of this change will be found under the tests for chromates (639–644).

For minerals containing Cr refer to par. 1419.

REACTIONS OF CHROMIUM.

Use Chrome alum, $CrK(SO_4)_2.12H_2O$.

282. **AmOH** : pale bluish-green or purple precipitate, $Cr(OH)_3$. If AmOH is added in large quantity and the liquid is heated, some of the precipitate will dissolve, producing a beautiful violet-red solution. The colour of the liquid is best seen after the precipitate has been removed from it by filtration. From this red solution the $Cr(OH)_3$ is reprecipitated when the liquid is boiled for several minutes in a porcelain dish.

283. **KOH,** if it is added in small quantity, gives the same precipitate, $Cr(OH)_3$. If more cold KOH is added, the precipitate is entirely dissolved to a green fluid. When this liquid is diluted with water and then boiled for several minutes, the $Cr(OH)_3$ is reprecipitated and the liquid becomes colourless. When AmCl is added to the KOH-solution, the $Cr(OH)_3$ is also reprecipitated.

284. **Am_2S** also precipitates $Cr(OH_3)$, H_2S gas being given off or remaining dissolved. See the equation in paragraph 267.

285. **Lead peroxide (PbO_2), or Red lead,** may be added to the green liquid which has been obtained by adding KOH in excess to the chromium solution (283). When this liquid is boiled with the lead oxide, its colour changes to yellow; a yellow precipitate ($PbCrO_4$) may then be thrown down from this yellow solution by adding to it $H\bar{A}$ in excess. This serves as a confirmatory test for the presence of Cr.

286. **A Solid substance containing Cr, if it is heated with fused Na_2CO_3 and potassium nitrate (KNO_3)** on platinum or porcelain, as is described in Exp. 25, par. 56, yields, when it is cold, a bright yellow mass containing sodium chromate (Na_2CrO_4).

When this cold product is dissolved in boiling water, a yellow liquid is obtained; if this solution is acidified with $H\bar{A}$ its colour reddens, and if it is then boiled for a few minutes in order to drive off CO_2, it gives with solution of lead acetate ($Pb\bar{A}_2$) a yellow precipitate of $PbCrO_4$.

287. **A Borax-bead containing Cr** is green after it has been fused either in the outer or in the inner blowpipe-flame.

DETECTION OF THE METALS IN GROUP III.A., WHEN THEY OCCUR TOGETHER.

288. **The following Differences** are utilised :—

1. The solubility of $Al(OH)_3$ in boiling KOH, in which $Fe(OH)_3$ and $Cr(OH)_3$ are insoluble.

2. The conversion of $Cr(OH)_3$ by fusion with Na_2CO_3 and KNO_3 into soluble Na_2CrO_4 : $Fe(OH)_3$, when it is thus treated, remaining as Fe_2O_3 which is insoluble in water.

3. Cr is then detected by the yellow colour of the aqueous solution of the resulting Na_2CrO_4, and by the formation of a yellow precipitate when this solution is acidified with $H\bar{A}$, and $Pb\bar{A}_2$-solution is added to it.

4. Fe is found by the blood-red coloration which is obtained, when KCNS is added to the solution in HCl of the Fe_2O_3 resulting from (2).

289. A Solution which may contain Al, Fe, Cr, is first examined for ferrous and ferric salts in the following manner :—

(**a**) To a few drops of the liquid, acidified with HCl, add a little K_4FeCy_6-solution : if a blue precipitate is produced, Fe is present : proceed to (**b**) ; if no blue precipitate forms, proceed to (**c**). This portion of the liquid is rejected.

(**b**) Two other small portions of the acidified solution are then tested ; one with freshly made solution of K_3FeCy_6 (*Note*, **279**), which, by giving a dark blue precipitate, would show the presence of $Fe^{\cdot\cdot}$; the other with KCNS-solution, which may cause a blood-red colour, proving the presence of $Fe^{\cdot\cdot\cdot}$. These portions of the liquid are rejected. Proceed to (**c**).

(**c**) The rest of the original solution is boiled, after a few drops of strong HNO_3 (**271**) have been added if ferrous salt is present. AmCl in volume equal to one quarter that of the solution is then added; then AmOH is gradually added, with constant stirring, until the liquid is just alkaline and smells faintly of NH_3. The liquid is now boiled and filtered, and the precipitate is examined by Table III.A. (**1255**), all the Notes appended to the Table being disregarded.

GROUP III.B.—ZINC GROUP.

290. This Group includes Zn, Mn, Ni, Co.

Compounds of these metals are not precipitated by the Group-reagents for Groups I., II., and III.A., and differ from those of metals of Groups IV. and V. by being precipitated from their neutral or alkaline solutions by yellow ammonium sulphide (*Note*), and from their alkaline solutions by H_2S. Mn is, however, gradually oxidised and precipitated, if its solution is mixed with AmCl and excess of AmOH and is then exposed to the air.

The compounds of the metals of this Group show no characteristic flame-

colorations; but, with the exception of those of Zn, they give characteristic colours to a borax-bead.

Finely-powdered barium carbonate ($BaCO_3$) does not precipitate the metals of Group III.B. from their solutions, as it does the metals of Group III.A., unless they are present as sulphates.

Note.—The *yellow* ammonium sulphide, which is repeatedly referred to in the tests for Ni and Co, is the reagent which is ordinarily found in the laboratory. It is a polysulphide of varying composition and may be represented by the general formula Am_2S_n. The monosulphide, Am_2S, and the ammonium hydrogen sulphide, AmHS, are colourless; they may be used as reagents unless *yellow* Am_2S or Am_2S_n is specified.

Zinc (Zn).

Density from 6·9 to 7·2, melting-point 419·4° C., boiling-point 916° C.

291. Zinc is a white metal which is somewhat ductile and malleable. In moist air it is slowly oxidised at ordinary temperature, and is eventually covered superficially with a film of basic carbonate. When the metal is heated to a high temperature in the air, it burns with a greenish light and is converted into ZnO.

The pure metal is practically insoluble in all acids, but ordinary commercial zinc is readily dissolved by acids and by boiling caustic alkali solution.

The zinc compounds correspond to the basic oxide ZnO, and the soluble salts contain a colourless, divalent ion.

For minerals containing Zn refer to par. **1419**.

REACTIONS OF ZINC.

Use Zinc sulphate, $ZnSO_4.7H_2O$.

292. Am_2S: white precipitate (ZnS). This precipitate often appears yellow, owing to the presence of excess of yellow ammonium polysulphide (Am_2S_n) in the liquid. The true colour is evident, as soon as the precipitate, produced by Am_2S_n, has been separated from the liquid by settling or by filtration.

The colour and the solubility of this precipitate are more satisfactorily ascertained when the precipitate is obtained as in the next paragraph (*Note*, **293**).

293. H_2S: white precipitate (ZnS). Zn is only partly precipitated from the neutral solution by H_2S, since H_2SO_4, in which ZnS is soluble, is formed during the reaction:—

$$ZnSO_4 + H_2S = ZnS + H_2SO_4$$

If, however, NaOH or AmOH has been added in sufficient excess to the zinc solution, it will form a clear solution (**294, 295**); and since free H_2SO_4 cannot exist in this alkaline liquid, the Zn may be entirely precipitated from it as sulphide by H_2S.

The addition of a sufficient quantity of solution of sodium acetate (Na$\bar{A}$) to the zinc solution also enables H_2S to effect complete precipitation of the Zn as sulphide, since acetic acid (H$\bar{A}$), in which ZnS is insoluble, replaces the H_2SO_4 in the solution :—

$$ZnSO_4 + H_2S + 2Na\bar{A} = ZnS + Na_2SO_4 + 2H\bar{A}.$$

Add to some $ZnSO_4$-solution AmCl, then AmOH until it is alkaline, and then H_2S. White ZnS will be precipitated. Add to separate portions of this liquid HCl, H$\bar{A}$, and Am_2S respectively; ZnS will be found to be soluble in HCl, but insoluble in H$\bar{A}$ and in Am_2S.

Note.—The tests which show the colours and solubility of the sulphides of the metals of this Group are best tried on the precipitate which is obtained by the addition of AmCl, AmOH in excess and H_2S to the solution of the metal, unless freshly prepared *colourless* Am_2S can be obtained; since the *yellow* polysulphide solution causes sulphur to precipitate together with the metallic sulphide :—

$$ZnSO_4 + Am_2S_2 = ZnS + S + Am_2SO_4$$

and the sulphur, thus precipitated, is not dissolved by the solvents of the metallic sulphide. Sulphur is also precipitated on the addition of acid to the liquid containing the precipitate together with an excess of Am_2S_n, and this further complicates the results :—

$$Am_2S_n + 2HCl = 2\,AmCl + H_2S + S_{n-1}.$$

294. **KOH,** added in small quantity, gives a white precipitate, $Zn(OH)_2$. The addition of more KOH causes this precipitate to dissolve, owing to the formation of a soluble alkaline zincate :— $Zn(OH)_2 + 2KOH = K_2ZnO_2 + 2H_2O$. When much water is added to this solution and the liquid is boiled, the $Zn(OH)_2$ is reprecipitated. The Zn may also be precipitated from the KOH-solution as ZnS by the addition of H_2S.

295. **AmOH,** if added in small quantity, yields a precipitate of $Zn(OH)_2$, which readily dissolves in excess : the formation of this precipitate is prevented by the previous addition of AmCl.

296. **Blowpipe-test on Charcoal.**—Mix some finely-powdered $ZnSO_4.7H_2O$ and Na_2CO_3 in a small cavity on wood-charcoal, and heat the mixture in the inner blowpipe-flame.

An incrustation will be obtained on the charcoal, which is *yellow* while hot and *white* when cold. (*Note.*) This deposit cannot be driven away by the outer blowpipe-flame, but it is easily removed when it is heated in the inner flame.

Moisten the cold incrustation with cobalt nitrate solution and heat it strongly in the outer blowpipe-flame; it will become *green*.

Note.—The above changes of colour are more distinctly seen when a little zinc oxide (ZnO) is heated in an ignition tube, or in the outer blowpipe flame on charcoal. The oxide will be *yellow* while it is hot and *white* when it has cooled. If the oxide is moistened on charcoal with cobalt nitrate

solution, and is then reheated in the outer blowpipe-flame, it will become *green.*

Manganese (Mn).

Density 8·0, melting-point 1225° C.

297. Manganese is a brittle grey metal, which is slowly oxidised superficially in the air, and decomposes water with evolution of hydrogen. It is attacked by dilute acids, even by acetic acid.

It forms six oxides, MnO, Mn_2O_3, Mn_3O_4, MnO_2, (MnO_3) and Mn_2O_7.

The most important compounds are the manganous compounds, which correspond to the basic oxide MnO (298–301); and the permanganates, which correspond to the acidic oxide Mn_2O_7 (604–607).

The former compounds contain a divalent pale-pink positive ion, and the latter a monovalent purple-red negative ion.

For minerals containing Mn refer to par. 1419.

REACTIONS OF MANGANESE.

Use Manganous chloride ($MnCl_2$), or Manganous sulphate ($MnSO_4$).

Manganous salts are usually of a *pale pink* colour, alkaline manganates are *green,* permanganates are *purple.*

298. Am_2S : flesh-coloured or pale pink precipitate (MnS). The true colour of this precipitate is only seen after it has been separated by filtration, if the ammonium sulphide was yellow.

The colour of the moist filtered precipitate changes by oxidation to dark brown, when it is allowed to stand in contact with the air.

For the solubility of this precipitate, refer to the next paragraph (*Note,* 293).

299. H_2S precipitates pale pink MnS, partially from neutral solutions and entirely from alkaline solutions, but it produces no precipitate in the presence of HCl or of HĀ.

Add to some $MnCl_2$-solution AmCl, AmOH in excess, and then H_2S ; and show with separate portions of the precipitate that MnS is soluble in HCl and in HĀ, but is insoluble in Am_2S.

300. KOH : white precipitate, $Mn(OH)_2$, insoluble in excess, and quickly turning brown by oxidation in the air. This change of colour is most rapid after the precipitate has been filtered off, since it is then exposed more fully to the air.

301. AmOH gives the same precipitate, $Mn(OH)_2$. If sufficient AmCl is first added, however, AmOH produces no immediate pre-

cipitate ; but if this alkaline liquid is exposed to the air, it gradually turns brown by oxidation, and the Mn is ultimately precipitated as a brown hydroxide.

302. **Blowpipe-test by Oxidation.**—When any solid substance containing Mn is heated *upon platinum foil* in the tip of the Bunsen-flame or of the outer blowpipe-flame, in contact with a fused mixture of Na_2CO_3 and KNO_3, the product yields a *bluish-green mass* when it cools.

The mixture of the substance with the alkaline salts should be heated by allowing the tip of the flame to touch the *under surface* of the foil, and the flame must not be allowed to come into contact with the surface of the mixture (Exp. 25, par. 56).

The test may also be made by fusing a mixture of Na_2CO_3 and KNO_3 into a bead in a loop of platinum wire, then taking up *very little* of the manganese compound upon the surface of the moistened bead, and fusing it into the bead by heating it in the extreme tip of the outer blowpipe-flame.

This reaction for the presence of manganese is very delicate, owing to the intensity of the colour of the manganate which is produced: therefore very little of the manganese compound should be used else the colour of the fused mass may appear almost black, and the result is then not characteristic.

303. **Blowpipe-test on Charcoal.**—When any manganese compound is heated with fused Na_2CO_3 on charcoal in the inner blowpipe-flame it yields a grey magnetic powder of Mn (60, 61).

304. **A Borax-bead** which contains *very little* Mn, will be *violet-red* while it is hot and *amethyst-red* when cool, after it has been fused in the outer blowpipe-flame. When the bead is heated in the inner blowpipe-flame it becomes *colourless*.

This reaction is very delicate, and yields a result with even minute quantities of manganese compounds Larger quantities of manganese render the bead opaque, after it has been heated in the outer blowpipe-flame.

Nickel (Ni).

Density 8·8, melting-point 1452° C.

305. Nickel is a hard, white magnetic metal, which does not alter in the air. It is dissolved slowly by hydrochloric acid and by sulphuric acid, and rapidly by nitric acid. The metal forms one series of compounds corresponding to the basic oxide NiO, and its soluble salts contain a green divalent ion.

For minerals containing Ni refer to par. 1419.

REACTIONS OF NICKEL.

Use Nickel sulphate, $NiSO_4.7H_2O$.

Hydrated nickel salts are usually *bright green* in colour : the anhydrous salts are yellow.

306. **Am_2S :** black precipitate (NiS).

Add more *yellow* ammonium polysulphide, warm and filter. The filtrate will be coloured brown by NiS, which has been dissolved by the excess of the polysulphide.

Pour this dark-coloured filtrate into a porcelain dish and boil it for some time, adding distilled water if necessary in order to prevent the liquid from evaporating to dryness. The dissolved NiS will be reprecipitated, and when it has been filtered off, the filtrate will be colourless.

If $H\bar{A}$ is added in excess to the dark-coloured filtrate, the dissolved NiS will also be reprecipitated.

For the solubility of NiS, refer to the next paragraph (*Note*, 293).

307. **H_2S :** black precipitate (NiS) in a neutral solution, or in a solution which contains no free acid except $H\bar{A}$ (293) ; HCl and other acids prevent the precipitation.

Add to some $NiSO_4$-solution AmCl, then AmOH in excess and then H_2S ; and show with the precipitate thus produced that NiS is insoluble in cold HCl and in $H\bar{A}$, but is dissolved when it is heated with HCl and a crystal of potassium chlorate ($KClO_3$).

308. **KOH :** light green precipitate, $Ni(OH)_2$, insoluble in excess.

309. **AmOH,** added in very small quantity, gives a bluish-green precipitate of basic salt. This precipitate is soluble in excess of AmOH to a violet-blue liquid : it is also soluble in AmCl.

If AmCl is first added to the $NiSO_4$-solution, the addition of AmOH causes no precipitate.

310. **Solution of Potassium cyanide (KCN),** if it is freshly-prepared by dissolving a small piece of solid KCN in water, and is added in small quantity to the nickel solution, gives a yellowish-green precipitate ($NiCy_2$). The further addition of the KCN-solution dissolves this precipitate as K_2NiCy_4, but the precipitate is reproduced when sufficient HCl is added to the solution.

311. **Precipitation as $Ni(OH)_3$ from K_2NiCy_4.**—Acidify some $NiSO_4$-solution with several drops of $H\bar{A}$; then add freshly-made KCN-solution gradually, while stirring or shaking the nickel solution, until the precipitate, which forms at first, is just redissolved.

Boil this solution for a short time: then cool it, and divide it into two parts.

The addition of HCl in excess to one part will produce a precipitate of $NiCy_2$, which often appears only after a time.

A black precipitate, $Ni(OH)_3$, will be formed on the addition to the other part, either of sodium hypochlorite solution (NaClO), or of potassium hypobromite (KBrO) :—$2K_2NiCy_4 + KBrO + 5H_2O = 2Ni(OH)_3 + KBr + 4KCN + 4HCN$. The hypobromite is conveniently prepared by adding to the nickel cyanide solution first KOH in excess, and then bromine water until the liquid remains yellow. The black precipitate forms more rapidly if the liquid is warmed.

312. **Blowpipe-test on Charcoal.**—When a mixture of finely-powdered nickel sulphate and Na_2CO_3 is heated on charcoal in the inner blowpipe flame, a grey powder of Ni will remain, which may be separated by levigation and shown to be attracted by the magnet (60, 61).

313. **A Borax-bead** containing Ni is *violet* or *reddish-brown* immediately after it has been fused in the outer blowpipe-flame, and it becomes *pale yellow* on cooling.

If the bead is heated for some time in the inner blowpipe-flame, it becomes *black* and *opaque*.

Cobalt (Co).

Density 8·9, melting point 1490° C.

314. Cobalt is a white, hard, magnetic metal, which closely resembles nickel in its properties. The compounds of cobalt correspond to the basic oxide CoO, and its soluble salts contain a pink divalent ion.

For minerals containing Co refer to par. 1419.

REACTIONS OF COBALT.

Use Cobalt nitrate, $Co(NO_3)_2.6H_2O$.

Hydrated or dissolved cobalt salts are usually *reddish-pink* in colour. The solid anhydrous salts are usually *blue* or *purple*. Cobalt iodide is green.

315. **Am_2S :** black precipitate (CoS). If yellow ammonium polysulphide is added, and the liquid is then boiled and filtered, the filtrate is coloured *yellow* by Am_2S_n; it is not dark coloured, since CoS, unlike NiS, is insoluble in yellow Am_2S_n. For the solubility of CoS refer to the next paragraph (*Note*, 293).

316. **H_2S :** black precipitate (CoS), forming only in alkaline solutions, or in solutions which contain no free acid except HĀ (293). The presence of HCl prevents the precipitation.

Add AmCl, then AmOH in excess, and then H_2S to some cobalt nitrate solution, and pour into two separate portions of this liquid HCl and HĀ respectively; the precipitate will not dissolve. To the portion containing HCl add a crystal of $KClO_3$ and heat; the precipitate will dissolve readily.

317. **KOH**: blue precipitate of a basic cobalt salt; if the liquid is warmed, or allowed to stand, the basic salt is decomposed, yielding the pink hydroxide $Co(OH)_2$, and this eventually becomes brown by oxidation into cobaltic hydroxide, $Co(OH)_3$.

318. **AmOH**: bluish-green precipitate, having the same properties as that produced by KOH. The precipitate is soluble in excess of AmOH and in AmCl, and is therefore not formed if AmCl is added to the cobalt-solution before AmOH, or if AmOH is added in excess.

319. **Freshly-prepared KCN-solution**, if it is added in small quantity, gives a reddish-brown precipitate ($CoCy_2$). When more KCN-solution is added slowly and while shaking the liquid, the precipitate dissolves as K_4CoCy_6, but the original precipitate reappears when HCl is added to the solution.

320. **Cobalticyanide reaction.**—Acidify some cobalt nitrate solution with a few drops of HĀ; then add freshly-made KCN-solution slowly, until the precipitate which forms at first is just redissolved.

Boil this liquid, then cool and divide it into two parts. Add to one of these portions HCl; and to the other either NaClO-solution, or excess of NaOH-solution followed by sufficient Br-water to render the liquid permanently yellow; no precipitate will appear in either case, even when the liquid is warmed (311).

This difference in behaviour of solutions of Ni and of Co, which have been boiled with excess of KCN, is due to the fact that $NiCy_2$ forms with KCN a compound (K_2NiCy_4) which is easily decomposed: whereas $CoCy_2$ forms with excess of KCN a similar compound (K_4CoCy_6), but this, in the presence of atmospheric oxygen, changes into the very stable compound K_3CoCy_6, potassium cobalticyanide, which resists decomposition by acids and by alkaline oxidising solutions:—

$$2K_4CoCy_6 + 2H_2O + O = 2K_3CoCy_6 + 2KOH + H_2O.$$

321. **Potassium nitrite (KNO_2)**, when it is added to solution of cobalt nitrate acidified with acetic acid, gives a golden yellow crystalline precipitate of potassium cobaltinitrite, $K_3Co(NO_2)_6$. If the solution is dilute, the precipitate only appears after a time, but its formation is hastened by rubbing the sides of the vessel with a glass rod. (Difference from nickel.)

322. **Blowpipe-test on Charcoal.**—When a solid cobalt compound is mixed with Na_2CO_3, and the mixture is fused on charcoal in the inner blowpipe-flame, it yields a grey magnetic powder of Co (60, 61).

323. **A Borax-bead,** which has been dipped into a strong solution of cobalt nitrate, assumes a *fine blue* colour when it is fused in either the inner or the outer blowpipe-flame. This colour is produced even by minute quantities of cobalt compounds.

DETECTION OF THE METALS IN GROUP III.B., WHEN THEY OCCUR TOGETHER.

324. **The following Differences** are made use of :—

1. The solubility of NiS in yellow ammonium polysulphide in which ZnS, MnS and CoS are insoluble.

NiS may then be reprecipitated by boiling this solution or by the addition of HĀ, and the presence of Ni may be confirmed by heating the NiS in a borax-bead (313).

2. The solubility of ZnS and MnS in cold dilute HCl, in which NiS and CoS are almost insoluble.

3. The solubility of $Zn(OH)_2$ in cold KOH, in which $Mn(OH)_2$ is insoluble.

White ZnS may then be precipitated from this alkaline solution by the addition of H_2S : and the $Mn(OH)_2$ may be heated in a fused mixture of Na_2CO_3 and KNO_3, when it will yield a bluish-green mass (302).

4. The difference in behaviour of the solution of $NiCy_2$ and of $CoCy_2$ in excess of KCN-solution, when the liquid is warmed with NaClO or with NaBrO (311, 320).

Another method for separating Ni and Co depends upon the fact that while Co is precipitated as $Co(OH)_3$ from its solution by $BaCO_3$ in the presence of Br, Ni is not precipitated by this means and remains in solution.

5. The marked difference in colour of the borax-bead containing Ni from that containing Co is a further means of detecting these metals.

Mn may be separated from Zn, Ni, and Co by passing H_2S into the neutral solution which has been mixed with sufficient NaĀ (293) ; Mn alone remains in solution (299), and the other metals are precipitated as sulphides.

325. **A Solution is Examined for Zn, Mn, Co, Ni,** by adding AmCl, then AmOH in excess, and then yellow Am_2S_n until the liquid smells of the sulphide after it has been well stirred or shaken.

The liquid is then heated, and a few drops of it are poured upon a filter. If the filtrate is colourless, sufficient Am_2S_n has not been added ; more Am_2S_n must then be added, and the liquid must be again heated and filtered, these processes being repeated until a coloured filtrate is obtained.

As soon as the filtrate is brown or yellow in colour, proving that Am_2S_n has been added in excess, the whole of the liquid is heated and filtered, and the precipitate is examined by Table III.B. (1257).

If the filtrate is yellow it is rejected, if it is brown it must be examined for Ni according to paragraph 1248.

REACTIONS OF THE RARER ELEMENTS IN GROUP III.

326. The rarer metals which are precipitated in the Am_2S group are *Be, *Ti, Ta, Nb [*Ce, *La, *Zr, *Th, *Y, Yt, Er, *Di], *In, *U, *V (Tl).

The metals whose symbols are included in square brackets are often called the "metals of the rare earths."

The reactions of those metals whose symbols are marked with an asterisk are described below.

The following metals are also precipitated as hydroxides or acids by AmOH:—$Be(OH_2)$, H_2TiO_3, H_3TaO_4, H_3NbO_4, $Ce(OH)_3$, $La(OH)_3$, $Zr(OH)_4$, $Th(OH)_4$, $Yb(OH)_3$, $Yt(OH)_3$, $Er(OH)_3$, $Di(OH)_3$; and if Am_2S is subsequently added, U, In, V and Tl are precipitated as $(UO_2)S$, InS, V_2S_3 and Tl_2S respectively.

$BaCO_3$, precipitated, or in finest powder, suspended in water is a useful reagent in this group.

Tl is often partially precipitated as chloride in Group I., and its reactions are given under that Group. V is not precipitated unless acid is added in excess, after Am_2S has been added.

BERYLLIUM (Be).—Use Beryllium sulphate, $BeSO_4.4H_2O$.

327. **Be occurs** as silicate in phenacite, and as silicate with aluminium silicate in beryl and in emerald. Be-salts in aqueous solution have an acid reaction and possess a sweet, astringent taste. The metal has a density of 2·1.

328. **Am_2S, AmOH; KOH, or NaOH** precipitates the flocculent hydroxide $Be(OH_2)$ which resembles $Al(OH)_3$ in appearance and in being soluble in KOH:—$Be(OH_2) + 2KOH = Be(OK)_2 + 2H_2O$. It differs from $Al(OH)_3$ in being precipitated from its solution in KOH by dilution and long boiling, and by the freshly-precipitated hydroxide being dissolved when it is boiled for some time with AmCl-solution.

329. **Alkaline carbonates** precipitate a carbonate, which is soluble in excess of the reagent; the carbonate is reprecipitated when this solution is diluted and boiled for some time; the solution and reprecipitation are most easily effected when Am_2CO_3 is used as the reagent. [Difference from $Al(OH)_3$.]

330. **$BaCO_3$**, suspended as fine powder in water, precipitates Be-solutions completely in the cold as $Be(OH)_2$.

331. **$H_2C_2O_4$ and Alkaline oxalates** produce no precipitate. (Difference from the metals of the rare-earths.)

332. **Moistened with Cobalt nitrate solution and heated** on charcoal in the outer blowpipe-flame, a *grey* mass is obtained. (Difference from Al.)

TITANIUM (Ti).—Use Titanium sulphate, $Ti(SO_4)_2$, or a solution of titanium hydroxide in hydrochloric acid.

333. **Ti occurs as TiO_2**, together with traces of Fe, Mn and Cr, in rutile, anatase, and brookite. TiO_2 occurs also in combination with Fe in titaniferous iron ore.

334. **Ignited TiO_2** is insoluble in water and in most acids: it is easily soluble in HF, less readily in boiling strong H_2SO_4: it forms $Ti(SO_4)_2$, which is soluble in *cold* water, after it has been heated with fused $KHSO_4$. TiO_2 differs from SiO_2 by not being volatilised when it is heated in a platinum dish with HF and strong H_2SO_4.

335. **By Dilution and long Boiling**, white flocculent hydrated TiO_2 is precipitated from solution of Ti in H_2SO_4 or in HCl, and from the cold aqueous solution prepared after treatment with fused $KHSO_4$ (334): the precipitate is metatitanic acid, H_2TiO_3: it cannot be filtered off until either an acid or AmCl has been added. This hydrolytic reaction is used to effect the separation of Ti from Al, Fe, Cr, and other substances.

336. **AmOH, KOH, NaOH, Am_2S, or $BaCO_3$**, white flocculent precipitate, insoluble in excess; if the precipitation and washing have been carried out in the cold, the precipitate is orthotitanic acid, H_4TiO_4, and dissolves in HCl and in dilute H_2SO_4. If the precipitation is made in hot solutions, almost insoluble metatitanic acid, H_2TiO_3, is precipitated.

337. **Zn or Sn** gives in strong and acid solutions a *blue* coloration; if the solution is dilute, a *rose-red* coloration is produced. The change of colour is due to the formation by reduction of coloured compounds, in which Ti is trivalent. The solution is preferably made acid with HCl.

338. **$Na_2S_2O_3$** precipitates Ti solution entirely when the liquid is boiled. (Difference from Fe.)

339. **Microcosmic-bead**: in the outer flame *yellow* while hot, *colourless* when cold: in the inner flame *yellow* while hot, *violet* when cold.

The production of these colours is promoted by introducing a minute fragment of Sn into the fused bead. The addition of a very small quantity of $FeSO_4$ causes the bead to become *blood-red* when it is heated in the inner blowpipe-flame.

CERIUM (Ce).—Use Cerous nitrate, $Ce(NO_3)_3$.

340. Ce occurs as silicate in cerite, orthite and gadolinite; also as phosphate in monazite sand.

Ce forms two oxides only, Ce_2O_3 and CeO_2, and both of these are basic. The cerous salts are white and are readily soluble in water. The ceric salts are orange-red, are insoluble or sparingly soluble in water, and are readily reduced to cerous salts by ordinary reducing agents: they are unimportant for ordinary purposes.

341. **AmOH or Am_2S**: white precipitate of $Ce(OH)_3$, insoluble in excess, but readily soluble in acids. The precipitate becomes yellow on exposure to air by formation of $Ce(OH)_4$. In the presence of H_2T the above reagents give no precipitate. (Distinction from Yt.)

342. **KOH**: white precipitate of $Ce(OH)_3$ turning yellow on exposure to the air.

343. **$H_2C_2O_4$ or $Am_2C_2O_4$**: white precipitate of cerous oxalate, insoluble in excess (Distinction from Zr), also insoluble in dilute mineral acids. White insoluble CeO_2 is formed when this precipitate is ignited.

344. **$BaCO_3$**: complete precipitation takes place on standing.

345. **KClO, KBrO, or $Am_2S_2O_8$**: a yellow or red precipitate on boiling, due to oxidation into ceric compounds.

346. **H_2O_2**, with sufficient AmOH to make the solution faintly alkaline, gives a dark orange precipitate of hydrated CeO_3. This is a most delicate reaction of cerium.

347. **K_2SO_4** produces a white crystalline precipitate of the double salt, $Ce_23SO_4.3K_2SO_4$ (Distinction from Be and Al), which is insoluble in a saturated solution of K_2SO_4. (Difference from Yt and Er.)

348. **Borax-bead**: outer flame, *red* while hot, *colourless* when cold; inner flame, *colourless*, but if CeO_2 is used a yellow opaque bead is obtained.

LANTHANUM (La).—Use Lanthanum nitrate, $La(NO_3)_3$.

349. La occurs in several minerals, but chiefly in gadolinite and monazite. It forms one oxide, La_2O_3, which is basic and forms colourless salts.

350. **AmOH, or Am_2S**: a white basic salt is precipitated which is difficult to filter.

351. **KOH**: white precipitate of $La(OH)_3$, insoluble in excess; unchanged by oxidising agents. (Distinction from Ce.)

352. **$H_2C_2O_4$, or $Am_2C_2O_4$**: white precipitate, insoluble in excess or in dilute mineral acids.

353. **Am_2CO_3**: white precipitate, insoluble in excess. (Distinction from Ce.)

354. **K_2SO_4**: white crystalline precipitate of $La_2(SO_4)_3.3K_2SO_4$, insoluble in concentrated K_2SO_4-solution.

La-compounds give no characteristic dry reactions.

ZIRCONIUM (Zr).—Use Zirconium sulphate, $Zr(SO_4)_2$.

355. Zr occurs mainly as zircon, $ZrO_2.SiO_2$. Zirconium forms two oxides, ZrO_2 and Zr_2O_5; the former is the more important.

Zr-sulphate may be obtained by fusing zircon with excess of Na_2CO_3, when sodium silicate and Na_4ZrO_4 are formed. On treatment with water the sodium silicate is dissolved, and the sodium zirconate is hydrolysed, leaving insoluble $Zr(OH)_4$:—$Na_4ZrO_4 + 4H_2O = Zr(OH)_4 + 4NaOH$. The $Zr(OH)_4$ is then washed and dissolved in dilute sulphuric acid.

356. **AmOH, KOH, or Am_2S :** white gelatinous precipitate of $Zr(OH)_4$, insoluble in excess, but readily soluble in dilute acids if it has been precipitated in the cold. If it is precipitated from a hot solution, it is difficult to dissolve in dilute acids, but is readily soluble in strong acids.

357. **Am_2CO_3 :** white precipitate of basic carbonate, soluble in excess, but reprecipitated when this liquid is boiled.

358. **$H_2C_2O_4$:** white precipitate of zirconium oxalate, readily soluble in excess and in $Am_2C_2O_4$-solution. (Distinction from Th and Ce.)

359. **$Na_2S_2O_3$:** complete precipitation as $Zr(OH)_4$ mixed with sulphur.

360. **Turmeric-paper,** after being moistened with the Zr-solution acidified with HCl, becomes reddened when it is dried. (Difference from Th.)

361. **Dry reaction.**—ZrO_2 becomes very luminous when it is heated in the blowpipe-flame.

THORIUM (Th).—Use Thorium sulphate, $Th(SO_4)_2$.

362. Th occurs as thorite, $ThSiO_4$, also mixed with other rare earths in gadolinite and monazite. Thorium salts correspond to the only oxide ThO_2.

363. **AmOH, KOH, or Am_2S :** white precipitate of $Th(OH)_4$, insoluble in excess, but readily soluble in dilute acids.

364. **Am_2CO_3 :** white precipitate of basic carbonate, readily soluble in excess, but reprecipitated from this solution when it is heated to 50° C.

365. **K_2CO_3 or Na_2CO_3 :** white precipitate of the carbonate, readily soluble in excess; this solution of the precipitate becomes turbid when it is boiled, but becomes clear again as it cools.

366. **$BaCO_3$** completely precipitates thorium salts in the cold.

367. **$H_2C_2O_4$:** white precipitate, $Th(C_2O_4)_2$, insoluble in excess and in dilute acids, but soluble in excess of hot $Am_2C_2O_4$-solution. From this hot solution of the double oxalate, HCl precipitates all the Th as oxalate. (Distinction from Zr.)

368. **K_2SO_4 :** white precipitate of $Th(SO_4)_2.2K_2SO_4.2H_2O$, difficultly soluble in water and insoluble in concentrated K_2SO_4-solution. (Difference from Yt.)

369. **HF, or KF :** white gelatinous precipitate, which becomes heavy and granular. (Difference from Al, Be, Ti, U and metals of the rare earths except Y.)

YTTRIUM (Yt).—Use Yttrium nitrate, $Yt(NO_3)_3$.

370. Yttrium is an important constituent of gadolinite, it is also present in cerite, thorite and monazite.

371. **AmOH, KOH, or Am_2S :** white precipitate of $Yt(OH)_3$, insoluble in excess.

372. **Am_2CO_3, K_2CO_3 or Na_2CO_3 :** white precipitate of yttrium carbonate, readily soluble in excess; after this solution of the precipitate has stood for a time an insoluble double salt precipitates.

373. **$H_2C_2O_4$** : white precipitate of the oxalate, insoluble in excess, difficultly soluble in HCl and slightly soluble in $Am_2C_2O_4$-solution.

374. **K_2SO_4** : no precipitate, since a double salt is formed which is soluble in excess of K_2SO_4-solution. (Difference from Ce, La, Zr, Th.)

375. **HF** : white amorphous precipitate, which becomes pulverulent when it is warmed. (Difference from Al, Be, U, Ti and metals of the rare earths except Th.)

INDIUM (In).—Use Indium sulphate, $In_2(SO_4)_3$.

376. **Indium occurs** in zinc-blende and in wolfram: it is a white malleable metal of 7·42 density.

377. **Alkaline hydroxides** precipitate white, voluminous $In(OH)_3$, which is insoluble in excess. Indium solutions are also precipitated by alkaline carbonates, by Na_2HPO_4, by boiling their neutral solutions with excess of NaÃ, by $BaCO_3$, and by alkaline oxalates.

378. **H_2S** gives no precipitate in strong and acidified solutions; in dilute and feebly acid solutions a little sulphide separates; in a solution, containing no free acid but HÃ, the metal is entirely precipitated as *yellow* sulphide, In_2S_3. This precipitate is insoluble in cold Am_2S, but dissolves when the Am_2S is boiled: *white* indium sulphide separates as the hot solution cools.

379. **Am_2S**, added after $H_2\bar{T}$ and excess of AmOH, gives a white precipitate of In_2S_3, which is soluble in Am_2S; the white precipitate becomes yellow when it is treated with HÃ.

380. **Flame-Coloration** : bluish-violet. The spectrum shows a very characteristic blue line (Fig. 51, p. 50); when indium chloride is introduced into the flame this line is brilliant, but it very rapidly disappears.

381. **Heated on charcoal with Na_2CO_3** : white malleable globules of In are obtained.

URANIUM (U).—Use Uranyl nitrate, $(UO_2)(NO_3)_2$.

382. **U occurs in nature** principally as *pitchblende*, U_3O_8; also as *uranite*, a hydrated uranium calcium phosphate; and as *chalcolite*, hydrated uranium copper phosphate.

The metal is heavy, having a density of 18·68.

Although salts of uranium corresponding to the oxide UO_2 are known, they are extremely unstable and change on exposure to air into *uranyl* (UO_2) salts. The oxide UO_2 acts as a divalent basic radicle in the stable uranyl salts, and the reactions described below are those of the uranyl compounds. All uranyl compounds are yellow or green in colour.

383. **AmOH, KOH, or NaOH** : yellow precipitate of uranate, $Am_2U_2O_7$, insoluble in excess.

384. **Am_2S** gives in neutral solutions a *dingy yellow* or *brown* precipitate of uranyl sulphide (UO_2S), which differs from ZnS, MnS, and FeS by being soluble in Am_2CO_3. The precipitated sulphide settles slowly, unless AmCl is added; it is soluble in acids, even in HÃ; when it is heated with Am_2S in excess, it is changed into black uranous oxide (UO) and sulphur.

H_2S produces no precipitate in acid solutions of uranyl salts.

385. **Am_2CO_3, $KHCO_3$, or $NaHCO_3$:** yellow precipitate of double carbonate, easily soluble in excess; from this solution the uranium is reprecipitated by the addition of NaOH or KOH, or by boiling the liquid; it differs in this respect from the corresponding iron precipitate.

386. **Na_2HPO_4 :** yellowish-white precipitate of UO_2HPO_4; in the presence of AmĀ, uranyl ammonium phosphate ($UO_2\,Am\,PO_4$) is precipitated.

387. **K_4FeCy_6** gives, in acid solutions, a reddish-brown precipitate of $(UO_2)_2FeCy_6$, which differs from the similar precipitate produced in a copper solution by dissolving in excess of AmOH to a *yellow* liquid. This is a very delicate test.

388. **$BaCO_3$** causes complete precipitation as uranyl barium carbonate, $Ba_2UO_2(CO_3)_3$. even in the cold.

389. **Zn** changes the *yellow* colour of acid solutions to *green.*

390. **Borax and Microcosmic beads :** after being heated in the outer flame, *yellow,* and in the inner flame, *green.*

VANADIUM (V).—Use Sodium vanadate, $NaVO_3$.

391. **V occurs** in vanadinite, $3Pb_3(VO_4)_2.PbCl_2$, and in certain iron-ores and copper-ores; also in many clays and in most granites. Vanadium is known in several stages of oxidation; it is usually found in analysis as vanadic acid or a vanadate, which corresponds to the oxide V_2O_5. In acid solution the vanadates are yellow or reddish in colour.

392. **Reducing agents :** H_2S, H_2SO_3, or $H_2C_2O_4$, reduces an acid solution of a vanadate to a divanadyl compound, and causes the colour of the solution to change to *blue*; with H_2S a deposit of sulphur is also formed.

393. **Zn,** when it is introduced into a very dilute solution, which is acidified with H_2SO_4 and is then gently warmed, causes the liquid to change in colour to *blue,* then to *green,* and then to *lavender-blue.* The changes of colour are due to successive stages of reduction.

394. **Am_2S,** if added in excess, gives a brown liquid containing sulpho-salts; the addition of an excess of acid to this brown liquid produces a *brown* precipitate of V_2S_5; the brown precipitate is redissolved by alkaline hydroxides and by Am_2S, forming a reddish-brown solution.

395. **Solid AmCl,** if it is added to the solution until it is saturated, precipitates Am_3VO_4 which is insoluble in saturated AmCl-solution.

396. **H_2O_2,** when it is shaken up with an acid solution, imparts to it a red colour; the colour is not removed by shaking the liquid with ether. This is a very delicate test.

397. **Borax-bead :** in the outer flame *colourless,* or *yellow* if much V is present: in the inner flame *green* hot and cold, or, if much V is present, *brown* hot and *green* cold.

DETECTION OF THE RARER ELEMENTS IN GROUP III.

398. **For the Detection of the Rarer Elements of Group III.** in the ordinary course of analysis, refer to the third and fourth columns in the Tables in pars. 1323, 1324.

GROUP IV.—BARIUM GROUP.

399. This Group includes Ba, Sr, Ca.

Analytically these metals differ from those of Group V. by being precipitated as carbonates by Am_2CO_3, and as oxalates by $Am_2C_2O_4$, in the presence of AmCl. They are not precipitated by any other Group-reagent. The carbonates are soluble in boiling solution of AmCl.

Barium Group of Metals.

400. The metals of this Group are difficult to isolate, and they oxidise rapidly when they are exposed to the air. Their compounds correspond to the oxide MO. Their hydroxides are soluble and alkaline and are strongly basic. The soluble salts which correspond to the strong acids are neutral, and they contain a colourless divalent ion.

The metals are often termed the "metals of the alkaline earths," since the oxides produced from the natural carbonates are alkaline to test-paper when they are dissolved.

REACTIONS OF BARIUM (Ba).

Use Barium chloride, $BaCl_2.2H_2O$.

For minerals containing Ba refer to par. 1419.

401. **Am_2CO_3**, added after AmCl, causes a white precipitate ($BaCO_3$). This precipitate is at first flocculent; but it slowly shrinks in volume and becomes crystalline, if the liquid which contains it is gently heated and is then allowed to stand. Prove that this precipitate is soluble in $H\bar{A}$.

402. **$CaSO_4$, or H_2SO_4**, causes a heavy white precipitate ($BaSO_4$), which is insoluble in HCl even when the liquid is boiled.

403. **K_2CrO_4**, added after some $H\bar{A}$, produces a yellow precipitate ($BaCrO_4$), which is soluble in warm HCl, but differs from $SrCrO_4$ by being insoluble in warm $H\bar{A}$.

404. **Hydrofluosilicic acid, H_2SiF_6**, produces a semi-transparent precipitate ($BaSiF_6$). The precipitate does not appear in dilute solutions until after some time; its formation is hastened by boiling, shaking, or stirring the liquid, or by adding alcohol. H_2SiF_6 yields no precipitates with solutions containing Sr or Ca.

405. **Ammonium oxalate, $Am_2C_2O_4$**, produces a white precipitate (BaC_2O_4).

406. **Flame-coloration :** $BaCl_2$ gives a yellowish-green colour to the flame, which is visible through the indigo-prism.

The barium-spectrum (Fig. 51, p. 50) consists of a number of lines, the most characteristic of which are three green lines, α, β, γ.

REACTIONS OF STRONTIUM (Sr).

Use Strontium nitrate $Sr(NO_3)_2.4H_2O$.

For minerals containing Sr refer to par. 1419.

407. $\mathbf{Am_2CO_3}$, added after some AmCl, gives a white precipitate ($SrCO_3$), which is soluble in HĀ. This precipitate is flocculent at first; but it gradually becomes crystalline and shrinks very considerably at ordinary temperatures, and more rapidly when it is heated.

408. $\mathbf{CaSO_4}$, or $\mathbf{H_2SO_4}$, gives a white precipitate ($SrSO_4$). This precipitate does not usually form in a cold solution at once, but only after some time. The precipitate, however, appears at once when the liquid is boiled.

409. $\mathbf{K_2CrO_4}$, added after some HĀ, causes no precipitate, since $SrCrO_4$ is soluble in HĀ.

410. $\mathbf{Am_2C_2O_4}$ produces a white precipitate (SrC_2O_4).

411. **Flame-coloration :** crimson-red; this colour appears intense red through the indigo-prism, unless the flame-coloration is very faint.

The strontium-spectrum contains many lines (Fig. 51, p. 50). The most characteristic are the orange line (α), the red lines (β, γ), and the blue line (δ).

REACTIONS OF CALCIUM (Ca).

Use Calcium chloride, $CaCl_2.6H_2O$.

For minerals containing Ca refer to par. 1419.

412. $\mathbf{Am_2CO_3}$, added after AmCl, gives a white precipitate ($CaCO_3$) which is soluble in HĀ. This precipitate is flocculent at first; but it shrinks considerably and becomes crystalline after a time, more rapidly when it is gently heated.

413. $\mathbf{CaSO_4}$ **:** no precipitate, even when the liquid is allowed to stand, or is boiled.

414. $\mathbf{H_2SO_4}$ **:** a white precipitate ($CaSO_4$) forms at once in

strong solutions, and often in weak solutions when they are boiled; but some $CaSO_4$ will always remain dissolved, since it is not quite insoluble in water.

Prove this by boiling the liquid, in which the further addition of H_2SO_4 has caused no precipitate and which contains the precipitate, and filtering it. Then keep adding AmOH to the filtrate and stirring it, until a drop of the solution turns turmeric-paper brown and the liquid smells of NH_3. Then add $Am_2C_2O_4$; a white precipitate will form, showing the presence of Ca (416) in solution as $CaSO_4$.

415. **K_2CrO_4 :** no precipitate.

416. **$Am_2C_2O_4$:** white precipitate (CaC_2O_4), soluble in most acids, but insoluble in HĀ and in oxalic acid, $H_2C_2O_4$.

417. **Flame-coloration :** yellowish-red; when this coloration is viewed through the indigo-prism it does not appear red, and differs in this respect from that given by Sr.

In the calcium-spectrum (Fig. 51, p. 50) the most characteristic lines are the green line (β) and the intense orange line (α).

DETECTION OF THE METALS IN GROUP IV., WHEN THEY OCCUR TOGETHER.

418. **The following Differences** presented by the solutions of these metals are made use of :—

1. Their different flame-colorations, which are examined if necessary through the indigo-prism and by means of the spectroscope.

2. The difference in the behaviour of their solutions with $CaSO_4$-solution, which at once indicates the presence or absence of Ba, or of Sr in the absence of Ba.

3. The insolubility of $BaCrO_4$ in HĀ, and hence the possibility of separating Ba, if present, by adding HĀ and then K_2CrO_4.

4. The fact that Sr, but not Ca, can be precipitated by $CaSO_4$ on boiling. This reagent will therefore indicate the presence of Sr in the absence, or after the separation of Ba.

5. The complete precipitation of Sr, if present, by boiling the solution with H_2SO_4; sufficient $CaSO_4$ still remaining in the filtrate to give a precipitate on the addition of AmOH in excess and of $Am_2C_2O_4$.

A Solution which has to be Examined for Ba, Sr, and Ca, and which can contain only these metals, is first made alkaline,

if it is not already so, by the addition of AmOH in excess. Am_2CO_3 is then added, and the addition of this reagent is continued as long as it causes any further precipitate after the liquid has been warmed, stirred well and allowed to settle. The liquid is then filtered.

A little more Am_2CO_3 is now added to the clear filtrate, and if this causes any further precipitate more Am_2CO_3 is added, and the liquid is again poured through the same filter. These processes are repeated, if necessary.

As soon as the filtrate gives no further precipitate with Am_2CO_3, all the metals of this Group, which were present in the solution, will have been precipitated as carbonates, and will remain on the filter after the filtration of the liquid.

The precipitate is then examined by par. 1260, and by Table IV. (1261), or by the simpler Table IV.A. (1262).

GROUP V.—THE POTASSIUM GROUP.

419. This Group includes K, NH_4, Na, Li, Mg, together with the rarer metals Rb, Cs.

The members of this Group are not precipitated from their solutions by any Group-reagent.

The reactions of the rarer metals, Rb and Cs, are given in pars. 446, 447.

The Alkali Metals.

420. Li, Na, K, Rb and Cs are known as the alkali metals. The radicle ammonium is included in this analytical group because its compounds and their reactions closely resemble those of the alkali metals.

These metals are rapidly oxidised in the air, and are converted ultimately into their peroxides. They decompose water at ordinary temperatures with evolution of hydrogen and formation of strongly basic alkaline hydroxides.

Their compounds correspond to the oxide M_2O, and are usually colourless and soluble. The oxides are strongly basic. The solutions of the salts corresponding to the strong acids are neutral in

reaction, and solutions of salts corresponding to weak acids are alkaline in reaction.

The salts are usually somewhat volatile and impart distinctive colours to a non-luminous flame, which give characteristic and simple spectra.

Note.—The solution of H_2PtCl_6 which is used for the detection of some of these metals is commonly known as platinum chloride ($PtCl_4$) solution, but it actually contains chlorplatinic acid, H_2PtCl_6; both of these names and formulæ are used in the text.

REACTIONS OF POTASSIUM (K).

Use Potassium chloride, KCl.

For minerals containing K refer to par. 1419.

421. **Platinum chloride, or Chlorplatinic acid, H_2PtCl_6** (see *Note* above), if it is added to some of the KCl-solution on a watch-glass, and stirred gently but persistently with a glass rod, gives a yellow crystalline precipitate (K_2PtCl_6); this precipitate forms first along the lines where the rod has rubbed the glass.

Stir up the precipitate and pour off the liquid with the precipitate into three test-tubes.

To one of these portions add much distilled water and heat, the precipitate will dissolve. To another part add alcohol, the precipitate will not dissolve. Hence this precipitate is soluble in water and insoluble in alcohol.

By warming the third portion with solution of potassium hydroxide (KOH), the precipitate is shown to be soluble in that liquid.

Remarks.—Since this precipitate is soluble in alkalis, a liquid, to which this test has to be applied, should always be made neutral or faintly acid before H_2PtCl_6 is added. It is always well to acidify the liquid with dilute HCl, and to make sure by test-paper that it is slightly acid in reaction.

Further, since the precipitate is less soluble in alcohol than in water, the addition of alcohol often hastens the formation of the precipitate in dilute solutions.

Owing to the solubility of the precipitate in water, very dilute solutions must be evaporated nearly to dryness and cooled before the test is applied.

422. **Sodium picrate,** if it is added to a little KCl-solution on a watch-glass, gives golden-yellow needle-like crystals of potassium picrate when the liquid is stirred gently with a glass rod. The potassium solution should be neutral, or faintly alkaline, and free from ammonium salts. The reaction is promoted in a dilute solution by the addition of alcohol; it is not affected by the presence of acetic acid.

423. **Sodium hydrogen tartrate, $NaH\bar{T}$,** if it is added to some of the KCl-solution in a test-tube, gives a white crystalline precipitate ($KH\bar{T}$). The precipitate usually appears only when the tube is well shaken for some time, after the mouth of the test-tube has been closed with the thumb.

Shake up the precipitate, and pour it off with the liquid into four test-tubes.

Add to three of these different portions, water, KOH, and HCl respectively; on being shaken or warmed with each of these liquids, the precipitate will dissolve.

To the fourth portion add alcohol; the precipitate will not dissolve.

Remarks.—When the above test is used for the detection of potassium, the precipitate will not be obtained at once in dilute solutions; but its formation is much hastened by the addition of alcohol. Very dilute solutions must first be concentrated by evaporation.

The solution to be tested should be neutral or feebly alkaline in reaction. If it is strongly acid in reaction, the free acid should be neutralised by the addition of Na_2CO_3-solution; or, if the acid is volatile, it may be removed by evaporation. Feebly-acid solutions may be at once mixed with $NaH\bar{T}$. To an alkaline solution, tartaric acid ($H_2\bar{T}$) should be added until the reaction of the liquid is strongly acid.

424. **Flame-coloration** (62).—Dip a loop of platinum wire, which gives no colour to the flame, into some strong KCl-solution; or moisten the wire, and dip it into some finely-powdered KCl: then hold the loop in the flame.

A *pale-lilac* or *lavender* coloration will be seen, if the KCl is pure. Even if the flame is yellow to the naked eye, owing to the presence of Na, it will appear deep *crimson* when it is viewed through the thicker parts of an indigo-prism (Exp. 33, 62).

The flame-coloration due to potassium shows a spectrum of two lines, a *red* line (α) and a faint *indigo-blue* line (β); these lines are at the extreme ends of the spectrum (Fig. 51, p. 50): a faint continuous spectrum is also visible.

425. **Heat a little Solid KCl** in a small dry test-tube; or powder it finely, and heat it on a piece of platinum-foil. The KCl will melt, but it will only produce slight white fumes when it is heated very strongly. This proves that potassium salts are very slightly volatile even at a bright red heat.

The fused residue is often transparent and invisible; but its presence may always be detected by a slight crackling being heard, during the cooling of the foil or of the test-tube.

REACTIONS OF AMMONIUM (NH_4).

Use Ammonium chloride, NH_4Cl or AmCl.

426. **Potassium hydroxide, KOH,** if it is poured in excess

into some AmCl-solution, or upon the solid, and heated, causes ammonia gas to be given off :—

$$NH_4Cl + KOH = NH_3 + KCl + H_2O.$$

The ammonia is recognised :—

(a) By its pungent smell, which is that of common "smelling salts."

(b) By turning moistened red litmus-paper blue, or turmeric-paper brown.

Wet a small piece of the test-paper with distilled water, and place it along the end of a glass rod. Then hold the rod in the test-tube, taking great care not to bring the paper into contact with the liquid or with the sides of the tube. The change of colour mentioned above will take place.

(c) By yielding white fumes with an acid gas or vapour. Hence if a glass rod or stopper, wetted with strong HCl, HNO_3, or $H\bar{A}$, is held over the mouth of the test-tube, dense white fumes will be seen.

427. **Platinum chloride or Chlorplatinic acid, H_2PtCl_6** (see *Note*, 420), when it is stirred on a watch-glass with some AmCl-solution, gives a yellow crystalline precipitate (Am_2PtCl_6).

This precipitate is soluble in water and in KOH-solution, but is insoluble in alcohol. If it is boiled with KOH, NH_3 is evolved, and it is distinguished in this way from the similar potassium precipitate, K_2PtCl_6. The remarks in small type after paragraph 421 apply to this reaction also.

428. **Sodium picrate,** when it is stirred on a watch-glass with some AmCl-solution, gives golden-yellow needle-like crystals, which are soluble in much water (see 422).

429. **Sodium hydrogen tartrate, $NaH\bar{T}$,** when it is shaken for some time in a test-tube with AmCl-solution, gives a white crystalline precipitate, $AmH\bar{T}$.

This precipitate is soluble in water, in KOH, and in HCl, but is insoluble in alcohol. The remarks in small type in paragraph 423 apply to this reaction also.

430. **Flame-coloration.**—Pure AmCl gives no flame-coloration; but since ammonium salts almost invariably contain a trace of sodium, they usually impart a yellow colour to the flame.

431. **Heat a little Solid AmCl** on a piece of platinum-foil: it will be converted into vapour and will produce copious white fumes. These fumes are best seen when the foil is removed for a moment from the flame. The solid at last entirely disappears, showing that AmCl is completely volatile.

Repeat the experiment by heating a small piece of solid AmCl in a dry test-tube. The solid may be completely volatilised, and its vapour condensed as a white coating or "sublimate" on the upper part of the tube.

Some ammonium salts, such as the carbonate and nitrate, are decomposed by heat into gases; they are therefore volatilised without producing white fumes or a sublimate.

REACTIONS OF SODIUM (Na).

Use Sodium chloride, NaCl.

For minerals containing Na refer to par. 1419.

432. **Flame-coloration.**—NaCl gives an *intense yellow* colour to the flame. The colour is either invisible, or appears only pale blue, when it is viewed through the indigo-prism; it never shows the slightest tinge of red when it is seen through the thicker parts of the prism.

When the sodium coloration is examined by a small spectroscope, it gives a single yellow line (*a*) (Fig. 51, p. 50).

The yellow coloration of the flame which is produced by sodium is usually readily seen, even in the presence of other flame-colorations, since it is not easily masked. In any case the yellow spectrum line may always be detected, even when mere traces of sodium are present.

If both potassium and sodium are present, the potassium coloration is usually unseen, and the yellow coloration of sodium alone is visible. But when the flame is viewed through the indigo-prism, the crimson coloration of potassium is at once seen (62, Exp. 33). The lines of Na and K may also be distinctly separated from one another by means of the spectroscope.

433. **Heat a little Solid NaCl** in a dry test-tube or on platinum-foil: it will melt without producing white fumes, and will give slight fumes only when it is heated very strongly, showing that NaCl is very slightly volatile even at a bright red heat.

Magnesium (Mg).

Density 1·75, melting-point 750° C., boiling-point 1100° C.

434. Magnesium is a white metal, which slowly oxidises in moist air, and burns brilliantly to its oxide when it is kindled in the air. It is readily soluble in acids and slowly decomposes water with evolution of hydrogen.

The metal resembles the metals of the Barium, or alkaline earths group, (400) in its general chemical characters, but its oxide is less basic. Its compounds correspond to the oxide MgO, and its soluble salts contain a colourless divalent ion.

For minerals containing Mg refer to par. 1419.

REACTIONS OF MAGNESIUM (Mg).

Use Magnesium sulphate, $MgSO_4.7H_2O$.

435. Add AmCl, then AmOH, and then **Sodium phosphate, Na_2HPO_4 :** a white crystalline precipitate ($MgAmPO_4.6H_2O$) will be produced :—

$$MgSO_4 + AmOH + Na_2HPO_4 = MgAmPO_4 + Na_2SO_4 + H_2O.$$

If much water is present, this precipitate will form only when the liquid is warmed, or is well stirred or shaken : it is soluble in HCl and in other acids, but is insoluble in AmOH.

436. **KOH** gives a white precipitate, $Mg(OH)_2$, which is readily soluble in acids.

437. **AmOH** gives a white precipitate, $Mg(OH)_2$; but if AmCl is added before the AmOH, no precipitate is produced.

438. **Am_2CO_3** gives a white precipitate, $MgCO_3$, but only in strong solutions and on standing for some time. The previous addition of AmCl prevents the formation of this precipitate.

439. **Flame-coloration.**—Pure $MgSO_4$-solution gives no colour to the flame.

440. **Blowpipe-test.**—If a little solid magnesium sulphate is placed in a small cavity on a piece of wood-charcoal, and is then heated in the tip of the outer blowpipe-flame, it will shine brightly and will give a white unmelted mass of MgO. No white fumes will be seen, since MgO is not volatile.

If this white mass is allowed to cool and is moistened with several drops of cobalt nitrate solution, and is then again heated to whiteness for some time in the outer blowpipe-flame, it will assume a *delicate pink colour*. This colour will be readily seen when a piece of white paper is held near the cold residue on the charcoal.

REACTIONS OF LITHIUM (Li).

Use Lithium chloride, LiCl.

441. Li occurs frequently in mineral waters and in the ashes of plants, also in small quantities in the minerals lepidolite, triphane, and petalite : the metal has a density of 0·59, and a melting-point of 186° C.

Li salts resemble salts of the metals of the Barium Group by the difficult solubility of the carbonate and phosphate ; they differ from those of K and NH_4 by not being precipitated by H_2PtCl_6 or by NaHT̄ ; Li is readily distinguished from Na by its flame-coloration and its spectrum.

LiCl may be separated from KCl and NaCl by its insolubility in a mixture of equal volumes of absolute alcohol and dry ether.

442. **Sodium phosphate, Na_2HPO_4,** if it is added to the solution, which must not be too dilute and must be made strongly alkaline with NaOH, gives on boiling a white crystalline precipitate (Li_3PO_4) which settles quickly.

Traces of Li may be precipitated by adding Na_2HPO_4, and then NaOH until the liquid remains alkaline, evaporating to dryness and washing the residue with dilute AmOH.

This precipitate may be distinguished from the phosphates of Ba, Sr, Ca, and Mg by heating it on charcoal in the blowpipe-flame, when it will readily fuse and be absorbed by the charcoal support.

The diluted cold solution of Li_3PO_4 in HCl also gives no precipitate when AmOH is added in excess, but a white crystalline precipitate forms when the liquid is boiled. Also the phosphate precipitate, when it is moistened with HCl, gives the characteristic flame-coloration and spectrum (443).

443. **Flame-coloration** : this is *carmine-red* ; the spectrum (Fig. 51, p. 50) consists of an intense carmine-red line (α)

The flame-coloration is concealed by that of Na, but the presence of Na does not interfere with the spectrum, and the Na-coloration may be removed by viewing the flame through the thinner parts of the indigo-prism.

The lithium flame-coloration differs from that given by K by being either unable to penetrate the thick layers of indigo-solution in the indigo-prism, or by being much lessened in intensity by passage through the indigo.

Lithium silicate only gives the flame-coloration after it has been fused with $CaSO_4$; lithium phosphate requires to be first moistened with HCl.

DETECTION OF METALS IN GROUP V.

444. The detection of metals of this Group, when they occur together, depends upon the following differences :—

1. Mg is indicated with certainty by its precipitation, even in dilute solutions, by Na_2HPO_4 in the presence of AmCl and AmOH, and by its precipitation by KOH-solution.

2. Na can be found by its yellow flame coloration ; and K may be found by its lilac flame coloration, or in the presence of Na by a crimson flame-coloration being seen through the indigo-prism, or by its spectrum.

3. Li may be detected by its carmine-red flame-coloration, which is not readily seen through the indigo-prism, or in the presence of Na by its spectrum.

4. NH_4 may be detected by the evolution of NH_3 when the substance is boiled with KOH-solution.

5. The test for K by means of H_2PtCl_6, NaHT̄, or sodium picrate is only conclusive in the absence of NH_4. If NH_4 is present, therefore, it must be removed by ignition before K can be tested for by precipitation.

It will be found more convenient to use the scheme in paragraph 445 than the Table given in paragraph 1263, and it will generally

be unnecessary to try the confirmatory test (IV.) for K, since K may be detected with certainty by its flame-coloration and by its spectrum.

Sodium is rarely absent from any substance. The quantity of this metal which is present may be judged from the flame-coloration: unless the colour is intense, only a trace of sodium is present.

Lithium has been included in this scheme because its compounds are of fairly common occurrence, but it is usually classed amongst the rarer metals of the Group.

SCHEME FOR DETECTING K, NA, LI, NH_4, MG WHEN THEY MAY OCCUR TOGETHER IN SOLUTION.

445. The scheme includes the following three tests or experiments, and a fourth confirmatory test may also be made. If a solid is to be examined it may be dissolved in water, or if necessary in dilute HCl.

I. Dip a clean loop of platinum wire into the solution and hold it near the top of the Bunsen-flame, watching for some minutes to see if any initial coloration undergoes change. Note the flame coloration, and if necessary confirm its indications by observation of the spectrum (Fig. 51, p. 50):—

A lilac coloration indicates **Presence of K.**

A crimson coloration shows **Presence of Li.**

A yellow coloration proves **Presence of Na,** and if the colour appears deep crimson through the indigo-prism this shows also **Presence of K.**

II. Add to a small part of the solution, after dilution if Li has been found (442), AmCl, AmOH and Na_2HPO_4, stir the liquid well and allow it to stand

A white precipitate forms, showing **Presence of Mg.**

III. Boil some of the solution with excess of KOH-solution, and try whether NH_3 is evolved, by smelling, or if necessary by moist litmus-paper or strong HCl introduced on a glass rod (426): NH_3 is smelt, or the turmeric becomes brown, or white fumes are produced with the HCl, indicating **Presence of NH_4.**

[If Mg is absent a confirmatory test for Li may be made by adding Na_2HPO_4 to the above boiling alkaline liquid, when white Li_3PO_4 will be precipitated.]

IV. The presence of K may be confirmed, if NH_4 is absent, by precipitating another part of the solution with H_2PtCl_6 (421), sodium picrate (422) or $NaH\bar{T}$ (423).

If NH_4 is present it must be removed by evaporating some of the solution to dryness in a porcelain dish, igniting the residue on platinum-foil until no more fumes are evolved when the foil is removed from the flame, dissolving the residue by boiling the foil in a test-tube with a little water, and testing this solution, after concentration if necessary by evaporation, with one of the above reagents for detecting K (421–423).

REACTIONS OF THE RARER METALS IN GROUP V.

The rarer metals included in this Group are Rb, Cs.

RUBIDIUM (Rb), CÆSIUM (Cs).—Use RbCl and CsCl.

446. The metals Rb, Cs occur in small quantities in some mineral waters, in carnallite, and in a few minerals.

The compounds of Rb and Cs resemble those of K by being precipitated by H_2PtCl_6 and by $H_2\bar{T}$, and by giving a flame-coloration similar to that of K.

These metals differ from K by the greater insolubility in water of their chlorplatinates. When these have been precipitated together, K_2PtCl_6 can be dissolved away from Rb_2PtCl_6 and Cs_2PtCl_6 by boiling the precipitate with successive small quantities of water. The alums containing these metals show a similar difference in solubility in cold water.

447. **Flame-colorations.**—The flame-colorations given by these metals are not distinguishable from that given by K. Cs and Rb are, however, readily distinguished from one another and from other elements by their spectra (Fig. 51, p. 59).

The blue lines (α, β), given by Cs, are especially distinct and characteristic.

In the Rb-spectrum the indigo-blue lines (α, β) are very distinct, but the red lines (γ, δ) are most characteristic.

The chlorides are the most suitable salts for the spectroscope test.

448. **The metals Li, Rb, Cs** are most readily detected in this Group by means of their spectra.

For the detection of these metals in the ordinary course of analysis refer to the fifth column of the Table in paragraph 1323.

SECTION IV.

REACTIONS OF THE INORGANIC ACID-RADICLES.

460. Remarks on Acids and Acid-radicles.—Acids may be defined as compounds, which are resolved by solution in water into the positive ion $H^{\cdot}$, and a negative ion called the "acid-radicle" (81): the acid-radicle may be either an element or a group of elements. Thus HCl and HNO_3 are resolved by solution in water into $H^{\cdot} + Cl'$ and $H^{\cdot} + (NO_3)'$ ions respectively.

The replacement of the hydrogen in an acid by a metal produces a "salt."

A "strong" acid is ionised to a large extent when it is dissolved; a "weak" acid is ionised only to a small extent by solution.

Sulphuric acid, nitric acid, the halogen acids (except hydrofluoric) and a few others are the common strong acids. They yield a large number of metallic salts, and the salts which are formed by the action of these strong acids upon the strong bases are neutral in reaction.

The weak acids, such as hydrogen sulphide, carbonic acid, silicic acid, and boric acid yield fewer salts, and the salts formed by their action upon the strong bases are alkaline in reaction.

There are also acids of intermediate strength, such as phosphoric acid and sulphurous acid; the salts corresponding to these acids are also of an intermediate character.

461. Trying Reactions.—The reactions for the Acid-radicles are tried in the same way as those for the metals (83-87), a salt or other compound containing the radicle being employed. A salt of sodium, potassium or ammonium is usually preferred for this purpose, since these metals do not as a rule interfere with the reactions of their associated Acid-radicles.

462. Acid-radicle Groups.—The Acid-radicles are usually detected in the course of analysis by special tests. They cannot advantageously be precipitated in Groups, from which the members of each Group are subsequently separated and identified, as is the case with the Metals.

Accordingly the classification adopted for their reactions consists in placing together in a Group those Acid-radicles which some-

what resemble one another in their reactions; and then stating at the end of each Group the differences upon which the detection of its members depends, when the radicles occur together.

At the end of each Group the student may with advantage detect one or more of its members in an unknown substance, as he has already done with the metals.

GROUP I.—SULPHATE GROUP.

463. **This Group includes** sulphate (SO_4), selenate (SeO_4), and fluosilicate (SiF_6).

These acid-radicles are distinguished by yielding a precipitate, when $BaCl_2$ is added in the presence of hydrochloric acid.

Sulphate is the only commonly occurring acid-radicle which gives with $BaCl_2$ a precipitate insoluble in boiling HCl.

Fluosilicate resembles sulphate by its Ba-precipitate being only slightly soluble in boiling HCl, but it is also related to silicate and fluoride (645–657).

Selenate yields a precipitate of $BaSeO_4$ when $BaCl_2$ is added in the presence of cold HCl, but this precipitate differs from $BaSO_4$ and $BaSiF_6$ by being dissolved when it is boiled for some time with strong HCl (252).

SULPHATE, $(SO_4)''$.—Use $Na_2SO_4.10H_2O$.

464. **$BaCl_2$, or $Ba(NO_3)_2$**; white precipitate, $BaSO_4$, which remains undissolved when it is boiled with dilute HCl or HNO_3.

Note.—**$BaCl_2$ and $Ba(NO_3)_2$ are themselves insoluble** in strong HCl and in strong HNO_3. Care must therefore be taken not to mistake precipitates caused by these acids for a precipitate of $BaSO_4$. These precipitates are readily distinguished from $BaSO_4$ by their solubility in water.

Add a little $BaCl_2$- or $Ba(NO_3)_2$-solution to strong HCl or HNO_3. A white precipitate will be produced, consisting of $BaCl_2$ or $Ba(NO_3)_2$, which is insoluble in the strong acid. Now add much water, the precipitate will dissolve readily and completely in the water.

465. **Blowpipe-test on Charcoal.**—If a sulphate, or any solid substance containing sulphur, is mixed with solid Na_2CO_3, and the mixture is then heated on charcoal in the inner blowpipe-flame until the Na_2CO_3 fuses, Na_2S will be produced:—

$$Na_2SO_4 + 4C = Na_2S + 4CO.$$

The Na_2S thus produced may be readily detected by detaching the cold solid mass from the charcoal with the point of a knife, placing a portion of it upon a bright silver coin, and moistening it with a drop of water: after the moistened mass has remained upon the coin for a short time, it is rinsed off, a black stain (Ag_2S) will then be seen upon the part of the silver upon which the substance rested (481).

Another portion of the cool mass may be moistened with a drop of HCl: a fetid smell of H_2S will be observed, and a piece of paper moistened with $Pb\bar{A}_2$-solution and held above the substance will be blackened (480).

This test is evidently only of value for detecting a sulphate, when it is known that sulphur is not present in any other form in the substance to be tested.

It is also necessary that sulphur should not be introduced by the Na_2CO_3, or by the flame. Since coal-gas may contain sufficient sulphur to give the above reaction with pure Na_2CO_3, it is advisable to employ the flame of a spirit- or petroleum-lamp (5, 6), rather than that of a gas-burner, for this reaction.

466. **Hydrogen sulphate, or Sulphuric acid, H_2SO_4,** in the cold undiluted condition, slowly chars many organic substances: this change is rapid when the acid is heated. If the acid is dilute it may be detected by producing black charred stains on filter-paper, which has been spotted or marked with the liquid and has then been dried by heat.

Sulphuric acid has a strongly acid reaction to litmus, and evolves hydrogen when it is diluted and warmed with Zn.

The above properties are, however, also shown by some metallic sulphates and by the acid sulphates.

SELENATE $(SeO_4)''$. —The reactions for selenate have been already given (251–254) in Group II. for the metals. Selenate is classed in Group II. because it gives a precipitate with H_2S, after its solution in hydrochloric acid has been boiled.

SILICOFLUORIDE, or FLUOSILICATE, $(SiF_6)''$.—Use Hydrogen silicofluoride or Hydrofluosilicic acid, H_2SiF_6.

467. **$BaCl_2$**: white precipitate, $BaSiF_6$: this precipitate usually appears only when the solution is gently warmed, and differs in this respect from $BaSO_4$. It differs from $BaSeO_4$ (252) by being only slightly soluble in boiling HCl: it is insoluble in alcohol.

Allow this precipitate to settle and reserve it for the reaction in paragraph 469.

The above precipitate shows some resemblance to $BaSO_4$ since it is only slightly soluble in HCl, but it differs in appearance by being more or less transparent and crystalline. Silicofluorides differ also from sulphates by

giving no precipitate with $Sr(NO_3)_2$ or with $Pb(NO_3)_2$. Further, when their solutions are heated with excess of AmOH, they yield a flocculent precipitate of H_2SiO_3 and leave AmF in solution (655).

Silicofluorides also differ from sulphates by the following very distinctive reactions.

468. **KCl-solution**, when it is warmed with solution of silicofluoride, gives a very transparent gelatinous precipitate, K_2SiF_6: this precipitate is only visible after it has been allowed to settle for a time: it is insoluble in alcohol.

469. **Strong H_2SO_4**, if it is heated with a silicofluoride, causes HF to be given off, which may be detected by its etching action on glass (654).

This reaction is especially useful for ascertaining whether a precipitate, which has been produced by $BaCl_2$, consists of or contains $BaSiF_6$, and the precipitate from paragraph 467 may be tested by this process, as follows:—

The precipitate is allowed to settle: almost all the water is then poured off: the remainder of the water is shaken up with the precipitate and is at once poured into a watch-glass: the remaining water is then decanted, and the precipitate which remains on the glass is warmed for some time with strong H_2SO_4. After the glass has been washed and dried, it will be found to be corroded where the precipitate has rested.

The more delicate process described in par. 654 may be substituted, the precipitate, separated by decantation or by filtration and drying, being treated in a platinum or leaden cup.

470. $CaCl_2$ gives no precipitate. [Difference from fluoride (656).]

471. **Hydrogen silicofluoride, or Hydrofluosilicic acid, H_2SiF_6**, is a strongly acid liquid, which volatilises completely as $SiF_4 + 2HF$ when it is heated in platinum, and therefore etches a watch-glass if it is evaporated to dryness in the glass. It gives reactions 467 and 468.

DETECTION OF ACID-RADICLES IN GROUP I.

472. After the acid-radicle has been precipitated by the addition of $BaCl_2$, it may be identified by noting the following differences in the properties of the barium precipitate.

The precipitate of $BaSO_4$ differs from that of $BaSeO_4$ by being quite unaffected when it is boiled with HCl.

$BaSeO_4$ may be dissolved away from $BaSO_4$ by being boiled with HCl, and selenite may then be detected in solution by the tests given in paragraphs 246–250. When $BaSeO_4$ is heated on charcoal, it gives the peculiar smell of rotten horse-radish (253).

$BaSiF_6$ is distinguished by heating it with strong H_2SO_4, when HF is evolved, and etches glass (469). For other differences, see paragraphs 467, 468.

GROUP II.—CARBONATE GROUP.

473. **This Group includes** carbonate (CO_3), sulphide (S), sulphite (SO_3), thiosulphate (S_2O_3), hypochlorite (ClO), and nitrite (NO_2).

Salts which contain these acid-radicles evolve characteristic gases when they are acted upon by dilute HCl.

CARBONATE, $(CO_3)''$.—Use Na_2CO_3, or $CaCO_3$.

474. **HCl, $H\bar{A}$, $H_2\bar{T}$,** and almost any other acid, when it is poured upon a carbonate in a test-tube, causes colourless, almost inodorous carbon dioxide gas, CO_2, to escape with effervescence. This gas is recognised by its property of turning lime-water or baryta-water milky, owing to the production of an insoluble carbonate.

The Lime-water test may be tried in four ways, as is described below, attention being paid to the precautions which follow.

1. A glass rod which has been just removed from some perfectly clear lime-water, and which has a small drop adhering to its end, is introduced into the test-tube in which the carbon dioxide has been evolved; the drop will quickly become milky. Care must be taken not to allow the rod to touch the liquid or the inside of the tube. The milkiness is best seen when the rod is removed and the drop is held above a dead black surface.

2. Since carbon dioxide gas is much heavier than air, it will remain in the test-tube in which it has been liberated, if the tube is held erect and its mouth is loosely closed with the thumb. If the tube is then gradually inclined, the heavy gas may be poured into another test-tube containing lime-water, without allowing any liquid to flow out. On closing this tube with the thumb, and shaking the lime-water up with the gas, the liquid will become milky.

3. The acid may be poured upon the carbonate in a small beaker, which is immediately covered with a watch-glass the under surface of which has a drop of clear lime-water adhering to the middle: the drop will become milky.

4. If the CO_2 is given off in considerable quantity, it may be conducted into some lime-water contained in a separate tube. This is effected by either of the forms of apparatus which are shown in Fig. 56.

Precautions.—In testing for carbonate the following precautions must be attended to.

The milkiness, which is at first produced in the lime-water, gradually disappears when more of the gas is absorbed. Hence, if the lime-water does not become milky at once, it must be constantly watched, in order to avoid the risk of the milkiness not being observed before it has been removed by the further absorption of the gas.

If the addition of the first few drops of acid to the substance does not cause an effervescence, more acid should be added, since a carbonate may be simply converted into an acid carbonate by the action of a small quantity of acid, and no gas is evolved during that change.

FIG. 56.

APPARATUS FOR TESTING GAS EVOLVED.

If much water is present in relation to the carbonate, effervescence may not occur, since the gas may remain in solution: it may usually be removed from solution and detected by warming the liquid.

A powdered solid substance, which is being tested for a carbonate by HCl, should be first moistened with a few drops of water in order to drive out the air-bubbles entangled within it, since if these escaped on the addition of the acid they might be mistaken for a slight effervescence.

475. **$BaCl_2$, or $CaCl_2$** produces in a solution of carbonate a white precipitate, $BaCO_3$ or $CaCO_3$, which is soluble in dilute HCl or HNO_3 with effervescence (474).

ACID OR HYDROGEN CARBONATE, OR BICARBONATE.

476. **A Bicarbonate** is changed by heat into a normal carbonate with evolution of CO_2 and H_2O :—$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$.

Prove this by heating some sodium bicarbonate ($NaHCO_3$) in an ignition-tube; drops of water will condense, and CO_2 may be detected by lime-water (474).

Also drop some $NaHCO_3$ into boiling water in a test-tube; effervescence will take place, and the escaping gas will give rise to milkiness in lime-water.

477. **$MgSO_4$.**—A solution of bicarbonate, which has been made with *cold* water, gives no precipitate with $MgSO_4$-solution; but after the solution has been boiled it will contain a normal carbonate, and this will give a precipitate of white $MgCO_3$.

478. **$HgCl_2$-solution** yields with solution of bicarbonate a *red* precipitate; solution of *normal carbonate* yields a *yellow* precipitate with $HgCl_2$-solution.

479. **Hydrogen carbonate, or Carbonic acid** (H_2CO_3), can only exist in dilute aqueous solution, and the addition of sufficient lime-water to its solution causes a permanent milkiness.

Other substances in solution, however, yield a similar result; hence it is best to boil the liquid, and to pass the escaping mixture of steam and CO_2 into lime-water; the lime-water will become milky. Bicarbonates give the same result (476), but a residue of carbonate remains in the solution and may be detected by par. 474, or may be obtained by evaporation.

SULPHIDE, $(S)''$.—Use solid FeS, or solution of Am_2S.

480. **HCl, or H_2SO_4,** when it is poured upon many sulphides, produces H_2S, which may escape with effervescence or may partly

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Precautions.—In testing for carbonate the following precautions must be attended to.

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Other substances in solution, however, yield a similar result; hence it is best to boil the liquid, and to pass the escaping mixture of steam and CO_2 into lime-water; the lime-water will become milky. Bicarbonates give the same result (476), but a residue of carbonate remains in the solution and may be detected by par. 474, or may be obtained by evaporation.

SULPHIDE, $(S)''$.—Use solid FeS, or solution of Am_2S.

480. **HCl, or H_2SO_4,** when it is poured upon many sulphides, produces H_2S, which may escape with effervescence or may partly

or entirely remain in solution until the liquid is heated. This gas is detected by its fetid smell, resembling that of rotten eggs, and by its property of darkening $Pb\bar{A}_2$-solution by formation of PbS. or of turning nitroprusside solution purple (492).

The gas may be made to act upon the $Pb\bar{A}_2$-solution by the methods given for CO_2 (474, 1–4); or a small strip of filter-paper, moistened with the solution, may be introduced into the gas on the end of a glass rod. The paper strip should be attached to the rod by only half its length, so as to expose both surfaces of the lower part of the strip to the action of the gas.

Note.—This test is made much more delicate, if the filter-paper is moistened with a solution prepared by adding KOH to boiling $Pb\bar{A}_2$-solution, until the precipitate which is formed at first is just redissolved. The test-paper which has been thus prepared, becomes intensely blackened by H_2S.

481. **Ag.**—If solution of sulphide is dropped upon a bright silver coin, it produces a black stain, Ag_2S. This stain may be removed by rubbing the coin with moist lime.

A solid sulphide, which gives off H_2S on the addition of HCl, produces a black stain when it is placed upon a silver coin and is moistened with a drop of HCl.

482. **$Pb\bar{A}_2$-solution** gives with solution of sulphide a black precipitate, PbS. The use of the solution produced by adding KOH in excess to $Pb\bar{A}_2$-solution (480, *Note*) makes this test more delicate.

483. **Sodium nitroprusside, $Na_2FeCy_5NO_2$,** gives a purple colour even with a mere trace of dissolved sulphide; no colour is given with free H_2S, hence the solution should be made alkaline with AmOH or an alkaline hydroxide before the reagent is added.

484. **The formation of Thiocyanate** (694) may be employed as a very delicate test for a soluble sulphide. It depends on the detection by means of $FeCl_3$ of the thiocyanate, which has been formed by the action of KCN-solution upon the sulphide.

485. **Ignition.**—Free sulphur and many sulphides, when they are strongly heated in a test-tube, give a sublimate of sulphur in the form of brown drops or of yellow powder.

486. **Ignition in the Air.**—Free sulphur and many sulphides, when they are heated in a tube open at both ends and held obliquely in the flame, produce SO_2 gas. This gas may be recognised by its pungent smell, and by causing the colour of paper moistened with $K_2Cr_2O_7$-solution to change to bluish-green (490).

487. **Insoluble Sulphide, when fused with Na_2CO_3** in a covered porcelain crucible or in a hard glass ignition-tube, yields

soluble Na_2S, which may be detected by the above tests (480–483).

488. **Fusion with KNO_3**, or simply heating with strong HNO_3, converts a sulphide into a sulphate, which may be detected in solution by $BaCl_2$ (464).

489. **Hydrogen sulphide, or Hydrosulphuric acid (H_2S)**, either as gas or in aqueous solution, is easily recognised by its smell and by its action on lead acetate solution (480), or it may be mixed with AmOH-solution in excess and the liquid tested by pars. 481–484.

SULPHITE, $(SO_3)''$.—Use Na_2SO_3.

490. **HCl, or H_2SO_4**, when it is poured upon a sulphite and warmed, evolves SO_2 gas: this gas may be recognised by its pungent smell and by turning $K_2Cr_2O_7$-solution green.

A drop of the $K_2Cr_2O_7$-solution, hanging on the end of a glass rod, may be exposed to the gas (474, 1); or a small strip of filter-paper may be wetted with the bichromate solution and then attached by half its length to the rod, the other half hanging freely in the gas.

491. **$BaCl_2$**: white precipitate, $BaSO_3$: the formation of this precipitate is prevented by the presence of HCl, but a precipitate usually forms because the sulphite often contains traces of a sulphate.

When Cl-water or Br-water is added to the clear solution of $BaSO_3$ in HCl, $BaSO_4$ is formed and precipitated:—

$$BaCl_2 + H_2SO_3 + H_2O + Cl_2 = BaSO_4 + 4HCl.$$

492. **Nascent Hydrogen.**—The addition of sulphite solution to a mixture of HCl and Zn, which is giving off pure H, immediately causes an evolution of H_2S. The H_2S is detected by its smell, or by blackening a piece of filter-paper moistened with $Pb\bar{A}_2$-solution, or with $Pb(OH)_2$ dissolved in excess of KOH (480, *Note*), or with alkaline nitroprusside solution (492).

493. **Hydrogen sulphite, or Sulphurous acid, H_2SO_3**, exists only in solution. It may be detected by adding to the liquid a drop of $K_2Cr_2O_7$-solution, when the reddish colour of the dichromate will at once change to green.

Strong aqueous solution of hydrogen sulphite slowly evolves SO_2, and dilute solutions evolve SO_2 when they are heated: the escaping gas may be readily detected by its smell and by $K_2Cr_2O_7$-solution (490).

Since H_2SO_3-solution is readily oxidised to H_2SO_4 by contact with dissolved oxygen, its solution usually contains H_2SO_4 unless it has been recently prepared.

THIOSULPHATE, $(S_2O_3)''$.—Use solution of $Na_2S_2O_3.5H_2O$.

494. **HCl, or H_2SO_4,** causes no immediate change in the cold solution; but after a few seconds the acidified liquid becomes turbid, owing to the separation of finely-divided yellow S, and it then contains H_2SO_3 :—$H_2S_2O_3 = S + H_2SO_3$.

SO_2 from the H_2SO_3 may be recognised by its pungent smell, when the acidified liquid is heated; and it may be detected in the solution, by adding a few drops of $K_2Cr_2O_7$-solution, which changes colour to green.

495. **$FeCl_3$** gives a reddish-violet colour with solution of thiosulphate: this colour disappears after a short time in the cold, and immediately when the liquid is heated, the $FeCl_3$-solution at the same time loses its yellow colour since it is changed into $FeCl_2$.

496. **$AgNO_3$** gives a white precipitate, $Ag_2S_2O_3$, which becomes black after standing for a short time, or immediately when the liquid is heated, owing to the formation of Ag_2S :—

$$Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4.$$

The above precipitate, $Ag_2S_2O_3$, dissolves very readily in excess of the $Na_2S_2O_3$-solution, hence it is most easily obtained by dropping the thiosulphate solution into some $AgNO_3$-solution.

497. **Hydrogen thiosulphate, or Thiosulphuric acid** (**$H_2S_2O_3$**), is extremely unstable, rapidly separating into $S + H_2SO_3$ (494).

Hypochlorite, $(ClO)'$.—Use solution of Bleaching-powder, containing $Ca(ClO)_2$.

498. **HClO is evolved from a hypochlorite** when it is in the solid state or in strong solution; it is probably liberated by the action of the atmospheric carbon dioxide. The smell of the vapour thus evolved resembles that of Cl, but is less irritating to the nose.

499. **HCl, or H_2SO_4,** if it is added in excess, sets free Cl in the cold :—

$$Ca(ClO)_2 + 4HCl = 2Cl_2 + CaCl_2 + 2H_2O.$$

The chlorine gas may be recognised by its smell, by its yellowish colour, and by its power of bleaching a piece of moistened litmus-paper when the paper is held for a short time in the gas (474

1–4). If the Cl is small in quantity and remains dissolved, a piece of litmus-paper may be shaken up with the solution.

The bleaching of litmus is gradually produced by solution of hypochlorite, even without the addition of acid, by the nascent oxygen which is slowly liberated from the hypochlorite. When the hypochlorite solution is heated, or the litmus-paper moistened with the solution is exposed to the carbon dioxide of the air, the bleaching is hastened. On the addition of an acid, however, the bleaching of the litmus-paper immersed in the solution is extremely rapid.

500. **$Pb\bar{A}_2$** : if solution of hypochlorite is added in large quantity to $Pb\bar{A}_2$-solution, it gives a white precipitate; this precipitate becomes red and then *dark brown* (PbO_2) when the liquid is boiled for a short time.

When hypochlorite is heated with $MnCl_2$-solution, it also gives a *dark brown* precipitate of hydrated MnO_2.

501. **Hydrogen hypochlorite, or Hypochlorous acid, HClO,** is a yellow liquid with sweetish smell; it is very unstable, unless it is largely diluted. This acid bleaches litmus, and evolves Cl when it is warmed with HCl.

Nitrite, $(NO_2)'$.—Use KNO_2.

502. **Dilute H_2SO_4,** when it is warmed with nitrite, causes a reddish-brown gas with a characteristic smell to be evolved. The coloured gas is usually best seen by looking down the test-tube at a white surface.

503. **Cold $FeSO_4$-solution,** when it is added to solution of nitrite, causes the liquid to assume a dark colour: this colour becomes much more intense when cold dilute H_2SO_4 is added.

The dark coloured substance which is produced is a compound of NO with $FeSO_4$; the compound is decomposed when the liquid is boiled, and reddish-brown gas is evolved (**502**).

504. **Nitrous acid liberates Iodine from Potassium iodide.** The nitrous acid may be formed by the addition of acid to the nitrite.

Drop a little starch-powder into some cold water in a porcelain dish, and stir and boil the liquid for a short time: then cool the starch-solution, and add to it a few drops of KI-solution.

Add to this liquid some solution of nitrite, and then several drops of $H\bar{A}$: an intense blue colour will be produced. This is due to the combination of the starch with the iodine, which has been set free by the HNO_2.

The liquid will often appear black at first, and the blue colour will then only become visible when much water has been added.

This is a most delicate test if the liquid is quite cold. But the

presence of a nitrite is not proved if the colour is produced before the HĀ is added.

505. **Metaphenylene diamine** gives a very intense yellow coloration when it is added to a slightly acidified solution of a nitrite. This reaction is delicate and is not given by a nitrate.

506. **Hydrogen nitrite, or Nitrous acid** (HNO_2), is extremely unstable and decomposes rapidly into HNO_3, NO, and H_2O. Its solution therefore evolves reddish-brown gas when it is heated in the air (502). Nitrous acid also colours $FeSO_4$-solution (503), and liberates iodine from KI (504).

DETECTION OF THE ACID-RADICLES IN GROUP II.

507. **The Detection of these Acid-radicles,** when they occur singly, presents no difficulty.

Their detection, when they occur together, is often complicated, since most of the acids, which are formed on the addition of HCl to salts containing acid-radicles of this Group, react upon one another. Thus HClO oxidises HNO_2, H_2S, and H_2SO_3; and H_2SO_3 oxidises H_2S.

The analyst may often succeed, by a skilful use of the above reactions, in detecting these acid-radicles when they are mixed. But their detection in certain mixtures is a problem which is only soluble by careful consideration, and is not unfrequently insoluble.

SO_2 may be detected by $K_2Cr_2O_7$-paper: H_2S by lead acetate-paper: Cl by bleaching moist litmus-paper: nitrite by evolving reddish-brown gas. But CO_2 can usually only be detected in the presence of much SO_2 after removing the SO_2: this may be effected by passing the gases through hot $K_2Cr_2O_7$-solution, when the SO_2 will be absorbed, and the CO_2 which passes on may then be detected by lime-water.

GROUP III.—NITRATE GROUP.

508. This Group includes nitrate, chlorate, bromate and iodate.

The nitrates and chlorates resemble one another in many respects, more particularly in the fact that none of them are perfectly insoluble in water; hence no method of precipitating them is known.

The bromates and iodates are of comparatively rare occurrence, and only a few of their reactions are therefore described.

NITRATE, $(NO_3)'$.—Use KNO_3 and $Pb(NO_3)_2$.

509. **$FeSO_4$-solution gives a dark brown colour with Nitric acid :** the nitric acid is formed from the nitrate by the addition of H_2SO_4, and is changed by the action of $FeSO_4$ into nitrite, which then colours the $FeSO_4$ (503).

Add to some solution of nitrate, contained in a rather broad test-tube, about an equal volume of strong H_2SO_4. Mix the liquids well, and then cool the mixture by holding the tube in a stream of cold water.

Now pour some strong cold $FeSO_4$-solution in a gentle stream down the inside of the tube, which is held in an inclined position. A distinct layer of the $FeSO_4$-solution may thus with care be formed on the surface of the acid liquid. A *dark coloured* film or ring, which sometimes extends upwards, will appear at the surface of contact of the two liquids.

This coloured film is most easily seen when a piece of filter-paper is held between the tube and a bright flame or window, and the light is viewed through the tube and the paper. A mere yellow colour is often produced in the absence of a nitrate, and may be disregarded.

The test is made more delicate by cooling the liquid, since heat prevents or removes the dark colour. For this purpose the heating of the liquid by the mixture of the strong acid with the solution must be avoided as much as possible, and the tube may be allowed to stand in a beaker of cold water for a few minutes.

If much nitric acid is present, the dark colour often extends upwards as soon as the strong sulphuric acid is mixed with the $FeSO_4$-solution ; but the heat which is evolved by the dilution of the strong acid soon causes the NO to escape and to form a reddish-brown gas in the test-tube, and the liquid at the same time loses its dark colour.

510. **Copper :** when a few small scraps of Cu are dropped into some nitrate solution, and strong H_2SO_4 is added, reddish-brown gas will appear either at once or when the tube is warmed. If the colour is faint, it is best seen by looking down the tube at a white surface.

The liquid at the same time becomes blue from the production in it of copper nitrate :—

$$8HNO_3 + 3Cu = 2NO + 3Cu(NO_3)_2 + 4H_2O.$$

The NO which is evolved is a colourless gas, but it yields reddish-brown NO_2 by oxidation when it mixes with the air in the upper part of the vessel.

511. **Indigo solution,** if it is poured in a cold and dilute condition into cold nitrate solution, until the mixture becomes faintly but decidedly blue, retains its blue colour unchanged when SO_2 is passed into the liquid (*Note*, 519), or when freshly made H_2SO_3 solution is added. This reaction distinguishes a nitrate from a chlorate (519).

512. **Brucine:** if a little brucine is moistened on a watch-glass with a drop of strong H_2SO_4, an intense red colour is produced on adding a drop of solution of a nitrate. This reaction is very delicate.

513. **Reduction to Nitrite by Ignition:** ignition converts alkaline nitrate into nitrite: hence if solid nitrate is heated to redness with fusion mixture ($Na_2CO_3 + K_2CO_3$) on platinum foil for several minutes, a soluble alkaline nitrite is formed, which may be dissolved when it is cool by boiling the foil in water.

A portion of this solution may be proved to contain nitrite by the starch test (504).

Another portion may be acidified with HNO_3, and will be found to give no precipitate with $AgNO_3$. Compare with paragraph 521.

514. **Reduction to Nitrite by the action of Hydrogen:** nitric acid may also be reduced to nitrous acid by the action of nascent hydrogen.

Add dilute H_2SO_4 to some nitrate solution, and then add some freshly-made starch-solution containing KI: no colour will be produced, but when a fragment of Zn is dropped in, and hydrogen is evolved, the liquid will assume a deep blue colour (504).

515. **Fusion of a Nitrate on Charcoal** in the blowpipe-flame causes "deflagration"; that is to say, the surface of the charcoal burns rapidly with a slight hissing noise.

516. **Ignition of the Nitrate of a Heavy Metal,** in a glass tube closed at one end, causes the evolution of a reddish-brown gas with a characteristic smell (NO_2) and of oxygen:—$PbN_2O_6 = 2NO_2 + O + PbO$. The NO_2 is recognised by its colour and by its smell, and the oxygen is found by inflaming a glowing splinter of wood. Lead nitrate may be used in trying this experiment.

517. **Hydrogen nitrate, or Nitric acid, HNO_3,** has a strongly acid reaction. It gives with $FeSO_4$-solution a brown ring (509); and with Cu a reddish-brown gas and a blue solution (510).

When nitric acid is evaporated with quill-clippings it stains them bright yellow.

CHLORATE, $(ClO_3)'$.—Use $KClO_3$.

519. **Indigo solution,** if it is added in a cold dilute condition to a *cold* solution of chlorate until the liquid is coloured faintly but distinctly blue, loses its colour as soon as SO_2 is passed into the liquid, or when some *freshly-made* H_2SO_3-solution is added and the mixture is shaken. Difference from nitrate (511).

Note.—Since the presence of sulphuric acid must be avoided in this reaction, it is well to pass SO_2 gas into the liquid which is being tested. The gas may be most readily obtained from a bottle of liquid SO_2.

520. **Strong H_2SO_4,** when it is poured upon a little solid chlorate, becomes orange-red in colour, and when the liquid is shaken it evolves a bright yellow gas, ClO_2 :—

$$3KClO_3 + H_2SO_4 = 2ClO_2 + KClO_4 + K_2SO_4 + H_2O.$$

This gas has a smell somewhat resembling that of chlorine. It undergoes explosive decomposition when it is gently heated, and the acid mixture accordingly crackles and even detonates when it is warmed in the tube by the flame.

Caution.—This experiment may be dangerous, unless very little chlorate is used, and the mixture is then heated gently with the mouth of the test-tube turned away from the person.

521. **Ignition of Alkaline Chlorate evolves Oxygen and produces Chloride.**

$AgNO_3$-solution gives no precipitate with solution of a chlorate, if chloride is absent.

But if some of the solid potassium chlorate is heated in a test-tube, it will fuse and give off oxygen with effervescence, and the chlorate will be converted into chloride :—

$$KClO_3 = KCl + 3O.$$

The oxygen may be detected by holding in the tube a slip of wood with a spark at its end ; the spark will burst into a flame.

If the tube is then allowed to cool, and the residue is dissolved by heating it with water, a portion of the solution will yield no evidence of the presence of a nitrite (504).

Another portion of the solution will yield a white precipitate (AgCl) on the addition of $AgNO_3$; this precipitate will not dissolve in HNO_3 even on boiling, but will dissolve readily in AmOH (539) : it is therefore produced by the chloride which has been formed from the chlorate, and indirectly proves the presence of chlorate.

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Add dilute H_2SO_4 to some nitrate solution, and then add some freshly-made starch-solution containing KI : no colour will be produced, but when a fragment of Zn is dropped in, and hydrogen is evolved, the liquid will assume a deep blue colour (504).

515. Fusion of a Nitrate on Charcoal in the blowpipe-flame causes " deflagration " ; that is to say, the surface of the charcoal burns rapidly with a slight hissing noise.

516. Ignition of the Nitrate of a Heavy Metal, in a glass tube closed at one end, causes the evolution of a reddish-brown gas with a characteristic smell (NO_2) and of oxygen :—$PbN_2O_6 = 2NO_2 + O + PbO$. The NO_2 is recognised by its colour and by its smell, and the oxygen is found by inflaming a glowing splinter of wood. Lead nitrate may be used in trying this experiment.

517. Hydrogen nitrate, or Nitric acid, HNO_3, has a strongly acid reaction. It gives with $FeSO_4$-solution a brown ring (509); and with Cu a reddish-brown gas and a blue solution (510).

When nitric acid is evaporated with quill-clippings it stains them bright yellow.

CHLORATE, $(ClO_3)'$.—Use $KClO_3$.

519. Indigo solution, if it is added in a cold dilute condition to a *cold* solution of chlorate until the liquid is coloured faintly but distinctly blue, loses its colour as soon as SO_2 is passed into the liquid, or when some *freshly-made* H_2SO_3-solution is added and the mixture is shaken. Difference from nitrate (511).

Note.—Since the presence of sulphuric acid must be avoided in this reaction, it is well to pass SO_2 gas into the liquid which is being tested. The gas may be most readily obtained from a bottle of liquid SO_2.

520. **Strong H_2SO_4,** when it is poured upon a little solid chlorate, becomes orange-red in colour, and when the liquid is shaken it evolves a bright yellow gas, ClO_2 :—

$$3KClO_3 + H_2SO_4 = 2ClO_2 + KClO_4 + K_2SO_4 + H_2O.$$

This gas has a smell somewhat resembling that of chlorine. It undergoes explosive decomposition when it is gently heated, and the acid mixture accordingly crackles and even detonates when it is warmed in the tube by the flame.

Caution.—This experiment may be dangerous, unless very little chlorate is used, and the mixture is then heated gently with the mouth of the test-tube turned away from the person.

521. **Ignition of Alkaline Chlorate evolves Oxygen and produces Chloride.**

$AgNO_3$-solution gives no precipitate with solution of a chlorate, if chloride is absent.

But if some of the solid potassium chlorate is heated in a test-tube, it will fuse and give off oxygen with effervescence, and the chlorate will be converted into chloride :—

$$KClO_3 = KCl + 3O.$$

The oxygen may be detected by holding in the tube a slip of wood with a spark at its end; the spark will burst into a flame.

If the tube is then allowed to cool, and the residue is dissolved by heating it with water, a portion of the solution will yield no evidence of the presence of a nitrite (504).

Another portion of the solution will yield a white precipitate (AgCl) on the addition of $AgNO_3$; this precipitate will not dissolve in HNO_3 even on boiling, but will dissolve readily in AmOH (539): it is therefore produced by the chloride which has been formed from the chlorate, and indirectly proves the presence of chlorate.

A chlorate which does not yield a soluble chloride by ignition must be mixed with fusion-mixture before it is ignited for this test.

This reaction readily distinguishes a chlorate from a nitrate (513).

522. **When a Chlorate is heated on Charcoal** in the blow-pipe-flame it causes the charcoal to deflagrate.

523. **Hydrogen chlorate, or Chloric acid, $HClO_3$,** is an odourless liquid, which first reddens and then bleaches litmus-paper. When chloric acid is kept for some time, it changes into $HClO_4$, O, Cl, and H_2O. The same change occurs rapidly when the acid is heated.

DETECTION OF NITRATE AND CHLORATE.

524. There is little difficulty in distinguishing nitrate from chlorate when they occur separately.

But nitrate and chlorate, when they are present together, more or less interfere with one another's reactions. They may be detected in the absence, or after the removal of chloride and nitrite, by heating the solid substance strongly for a short time, and then testing for nitrite and chloride (513, 521).

The preliminary removal of nitrite may be effected by boiling the substance with excess of acetic acid; and chloride may be removed by precipitation with $AgNO_3$, which must, however, not be added in excess. It is evident that the portion of the solution, to which $AgNO_3$ has been added, cannot be used for the test for nitrate, but if Ag_2SO_4 is substituted for $AgNO_3$ this difficulty is avoided.

A method for detecting mixed nitrate and chlorate by the action of nascent hydrogen, produced by zinc-dust in the presence of alkaline hydroxide, and conversion into NH_3 and chloride, is given in paragraph 1287.

DETECTION OF NITRATE IN PRESENCE OF NITRITE.

525. Add to the solution about one gram of urea, and then slowly add dilute sulphuric acid; the nitrous acid will be destroyed :— $CO(NH_2)_2 + 2HNO_2 = 2N_2 + CO_2 + 3H_2O$. When the evolution of gas has ceased, ascertain if any nitrite remains in the solution by adding solution of KI and starch (504), and if necessary add more urea and heat until the complete destruction of nitrite is proved by the absence of blue coloration of the starch.

Then add a little metallic zinc; a blue coloration will now be produced if nitrate is present (514).

The solution of nitrite and nitrate may also be freed from nitrite by boiling it for several minutes with strong ammonium chloride solution :—$NaNO_2 + NH_4Cl = NaCl + 2H_2O + N$. The solution may then be examined for nitrate as is directed above.

BROMATE, $(BrO_3)'$.—Use $KBrO_3$.

526. **$AgNO_3$** : white crystalline precipitate, $AgBrO_3$, almost insoluble in HNO_3, but readily soluble in AmOH.

527. **$Hg_2(NO_3)_2$** : white precipitate of $Hg_2(BrO_3)_2$.

528. **H_2S**, or **H_2SO_3** : each of these reduces bromate to bromide :—

$$KBrO_3 + 3H_2S = KBr + 3H_2O + S$$
$$KBrO_3 + 3H_2SO_3 = KBr + 3H_2SO_4.$$

529. **Mineral acids** liberate bromic acid, which then decomposes with formation of Br, H_2O and O; or if a reducing agent is present HBr is formed, and this reacting with unchanged $HBrO_3$ liberates Br :—

$$HBrO_3 + 5HBr = 3Br_2 + 3H_2O.$$

530. **Dry reactions**: an alkaline bromate is converted by ignition into bromide and oxygen (521): other bromates are decomposed with evolution of bromine and oxygen.

When a bromate is heated on charcoal in the blowpipe-flame it causes deflagration.

IODATE, $(IO_3)'$.—Use KIO_3.

531. **$AgNO_3$** : white curdy precipitate, $AgIO_3$, readily soluble in AmOH, but soluble with difficulty in HNO_3.

532. **$BaCl_2$** : white precipitate, $Ba(IO_3)_2$, soluble with difficulty in dilute HCl and dilute HNO_3.

533. **$Hg_2(NO_3)_2$** : light yellow curdy precipitate, $Hg_2(IO_3)_2$.

534. **H_2S, H_2SO_3** : each of these reduces iodate to iodide (528).

535. **Dilute H_2SO_4** does not decompose iodate, but if reducing substances, such as H_2SO_3 or $FeSO_4$, are present, HI is produced and reacts with unchanged HIO_3, causing separation of iodine :—$HIO_3 + 5HI = 3I_2 + 3H_2O$.

536. **Dry reactions** : all iodates are decomposed by ignition; some of them lose O and are converted into iodides, others evolve both O and I. When an iodate is heated on charcoal it causes deflagration.

DETECTION OF BROMATE AND IODATE.

537. Bromates and iodates are not of common occurrence. They may be recognized by treatment with dilute H_2SO_4 in the presence of H_2SO_3 or $FeSO_4$ (529, 535), or they may be converted into bromides or iodides (528, 534) and identified as such (546 and 552 *et seq.*).

GROUP IV.—CHLORIDE GROUP.

538. **This Group includes** chloride, bromide and iodide.

These Acid-radicles closely resemble one another in many of their reactions. They are precipitated by $AgNO_3$ from their solutions, even after HNO_3 has been added in excess. In this respect they differ from all acid-radicles except cyanide, thiocyanate, ferrocyanide and ferricyanide; and these are easily distinguished by other means.

The elements are commonly known as the "halogens," and their salts as "halides" of the metals.

CHLORIDE, (Cl)′.—Use NaCl.

539. **$AgNO_3$**, when it is added to the solution of a chloride, gives a *pure white* precipitate of AgCl.

The precipitate collects into curdy masses when the liquid is heated or shaken: it rapidly turns violet in sunlight, and slowly darkens even in diffused daylight.

Shake up and pour off the liquid with the precipitate into several test-tubes.

Decant the water from one portion and warm the precipitate with HNO_3, it will not dissolve: to another portion of the precipitate add AmOH, it will readily dissolve: AgCl may also be shown to be soluble in KCN-solution and in $Na_2S_2O_3$-solution.

Warm another portion of the precipitate, from which the liquid has been decanted, with a little strong H_2SO_4; the acid will remain colourless and no violet vapour will be given off as is the case with AgI (552).

540. **Strong H_2SO_4**, when it is added to a solid chloride, causes colourless HCl to be given off: this gas may be recognised by fuming in the air, by reddening moistened blue litmus-paper, and by making a drop of $AgNO_3$-solution, acidified with HNO_3, milky (474, 1–4).

541. **MnO_2 and H_2SO_4.**—Mix together intimately some finely-powdered chloride and MnO_2, then add strong H_2SO_4 and warm the mixture: chlorine gas will be evolved:—

$$2NaCl + MnO_2 + 3H_2SO_4 = Cl_2 + MnSO_4 + 2NaHSO_4 + 2H_2O.$$

This gas is recognised by its power of bleaching a piece of moistened litmus-paper, which is introduced into the tube on a glass rod.

A very delicate way of making the test is to mix the substances in a small beaker, and then cover this with a watch-glass which bears on its under surface a piece of moistened litmus-paper; the mixture is then warmed and allowed to stand for some time, and the test-paper is occasionally examined in order to see if its colour has disappeared.

Moist starch is not coloured when it is held in the escaping gas: this distinguishes chloride from bromide, when they are examined by this test. Compare with paragraph 547.

Many samples of commercial MnO_2 evolve Cl when they are heated with

H_2SO_4. Hence unless the MnO_2 has been specially prepared by precipitation, or is known to give no Cl when it is heated with H_2SO_4, it must be heated with H_2SO_4 as long as any bleaching action is produced on moist litmus-paper held in the tube; the substance to be tested may then be added, and Cl may be again tested for while the mixture is being heated.

542. **Chromyl chloride test.**—An intimate mixture is made of a solid chloride with three or four times as much $K_2Cr_2O_7$, by rubbing the two substances together to a fine powder in a mortar. This mixture is then heated with strong H_2SO_4 in the tube or flask represented in Figure 56 (474), or in a Clarke's retort (Fig. 57).

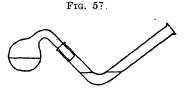
Reddish-brown vapour of chromyl chloride, CrO_2Cl_2, will be evolved :—

$$4NaCl + K_2Cr_2O_7 + 6H_2SO_4 = 2CrO_2Cl_2 + 4NaHSO_4 + 2KHSO_4 + 3H_2O.$$

If the vapour escaping from the delivery-tube is passed into some water, contained in a test-tube or in the bend of the condenser of Clarke's apparatus (Fig. 57), the water will become reddish-yellow in colour, owing to the formation of H_2CrO_4 :—

$$CrO_2Cl_2 + 2H_2O = H_2CrO_4 + 2HCl.$$

When excess of AmOH is added to the reddish-yellow liquid the colour will change to pale yellow, since Am_2CrO_4 is formed. But the original reddish-yellow colour will be reproduced when excess of $H\bar{A}$ is added; and the presence in this liquid of H_2CrO_4, and therefore of chloride in the original substance, may be proved by the formation of a yellow precipitate ($PbCrO_4$) on the addition of $Pb\bar{A}_2$-solution.

FIG. 57.

CLARKE'S RETORT.

Caution.—The detection of a chloride by this method depends on the formation of H_2CrO_4 by the action of the water in the tube on the vapour of CrO_2Cl_2. Great care must therefore be taken that none of the mixture containing chromate or chromic acid is allowed to pass into the delivery-tube and thence into the water, since if this occurred, chromic acid would be found even when no chloride was present.

Care must also be taken that the water is not sucked back into the hot strong H_2SO_4 when the apparatus shown in Fig. 56 is used. This is prevented by raising the delivery-tube out of the water as soon as the heating is stopped.

543. **Hydrogen chloride, or Hydrochloric acid, HCl,** is a colourless gas, which fumes in the air, and dissolves very readily in water, forming a strongly acid solution. Both the gas and its solution render $AgNO_3$-solution, which has been acidified with

HNO_3, milky. The solution of the acid evolves chlorine when it is heated with MnO_2, or with other oxidising substances.

544. **Chlorine** is a greenish-yellow gas with a suffocating odour. It dissolves in about one-third its volume of water, and the "chlorine-water" thus produced is pale yellowish-green in colour and possesses the general properties of the gas.

This solution probably undergoes change to a small extent:—$H_2O + Cl_2 \rightleftarrows HCl + HClO$, and the products ultimately formed, slowly in the dark, more rapidly in day- or sunlight, are HCl and O:—$H_2O + Cl_2 = O + 2HCl$.

Chlorine readily bleaches many moist vegetable colours, such as indigo and litmus, the bleaching being probably caused by the nascent oxygen produced as is shown by the above equation. Chlorine also liberates iodine from KI-solution, and the liquid becomes yellow or brown in colour.

$AgNO_3$-solution gives a white precipitate of AgCl with chlorine, but the precipitation is incomplete since soluble silver chlorate is simultaneously formed:—$3Cl_2 + 6AgNO_3 + 3H_2O = 5AgCl + AgClO_3 + 6HNO_3$.

545. **Chlorine and Hydrochloric acid** may be detected when they may be present together in solution as follows. After Cl has been found by its characteristic smell and bleaching power, the liquid is shaken up with mercury until the smell of Cl disappears and the liquid no longer bleaches litmus: insoluble Hg_2Cl_2 is formed and the liquid is therefore left neutral in reaction, if HCl was absent: an acid reaction of the liquid after the removal of chlorine therefore indicates the presence of an acid in the original solution, and hydrochloric acid may then be recognised by its characteristic tests (543).

BROMIDE, (Br)′—Use NaBr.

546. **$AgNO_3$**, when it is added to solution of a bromide, gives a *yellowish-white* precipitate (AgBr).

This precipitate is easily coagulated when the liquid containing it is heated or shaken; it is insoluble in HNO_3, easily soluble in KCN-solution and in $Na_2S_2O_3$-solution, and slightly soluble in AmOH. It resembles the precipitate of AgCl in these respects, but it is distinguished from AgCl by its yellowish colour, and by its slight solubility in AmOH.

If the liquid is decanted and the precipitate is heated with strong H_2SO_4, no violet vapour will be evolved as is the case with AgI (552).

547. **Strong H_2SO_4**, if it is heated with a bromide, causes the evolution of pungent acid fumes, HBr, which are accompanied and coloured by *reddish-brown* vapour of Br. This vapour somewhat resembles Cl in smell and by bleaching litmus, but it differs from Cl in colour.

The bromine vapour may also be recognised by its power of staining cold moist starch *orange-red*. The starch-powder may be

taken up on the wetted end of a glass rod, and then moistened by breathing upon it several times.

If MnO_2 is mixed with the bromide before H_2SO_4 is added, Br is evolved in greater quantity (541).

548. **Chlorine-water,** or solution of bleaching-powder which has been acidified with HCl, if it is added carefully drop by drop to solution of a bromide, liberates Br and this colours the solution orange-red.

The addition of Cl in excess must be carefully avoided, since Cl combines with Br and destroys its colour.

Warm a part of the coloured solution ; reddish-brown Br-vapour will be given off, and will stain cold moist starch *orange-red* (547).

Add carbon bisulphide (CS_2) to another portion of the coloured solution, and mix the liquids well by shaking them ; the Br will be dissolved away from the water by the CS_2, and if the liquids are allowed to stand at rest for a short time, the reddish-brown solution will sink beneath the colourless water.

If a little KOH-solution is now added and the liquids are shaken up together, the colour of the Br will disappear from the CS_2 ; this is due to the formation of the colourless salts KBr and $KBrO_3$, which remain in solution in the water :—

$$3Br_2 + 6KOH = 5KBr + KBrO_3 + 3H_2O.$$

549. **Evolution of Bromine on addition of H_2SO_4 and Chromate.**—If an intimate mixture of a solid bromide and $K_2Cr_2O_7$ is heated with strong H_2SO_4 in the apparatus shown in Fig. 57, page 147, reddish-brown bromine vapour will be evolved :—

$$6NaBr + K_2Cr_2O_7 + 11H_2SO_4 = 3Br_2 + Cr_2(SO_4)_3 + 6NaHSO_4 + 2KHSO_4 + 7H_2O.$$

The Br-vapour may be passed into water, and it will colour the liquid reddish-brown.

If CS_2 is then shaken up with part of this brown solution, it will dissolve away the Br and will settle beneath the colourless water as a brown layer.

If another part of the brown aqueous solution of Br is shaken with ÁmOH or KOH, the colour of the solution will be destroyed.

These reactions serve to detect a bromide in the presence of a chloride. Compare with paragraph 542.

550. **Hydrogen bromide, or Hydrobromic acid, HBr,** is a colourless, soluble gas, which fumes in the air and closely resembles HCl gas. Its aqueous solution differs from that of HCl by evolving coloured Br-vapour when it is heated with MnO_2.

551. **Bromine** is a heavy brown liquid which emits suffocating reddish-brown vapour.

Cold water will dissolve two and a half per cent. of Br, producing a reddish-brown solution known as "bromine-water." Br is readily identified by its smell, its colour, and its bleaching action, also by its solubility in CS_2, producing a deep reddish-brown liquid.

The detection of HBr and Br when they may be present together may be effected by a similar procedure to that described in paragraph 545.

IODIDE, (I)'.—Use KI.

552. **$AgNO_3$,** when it is added to solution of an iodide, gives a *yellow* precipitate, AgI.

This precipitate is easily coagulated when the liquid containing it is heated or shaken: it is insoluble in HNO_3, very slightly soluble in AmOH, but easily soluble in KCN-solution and in $Na_2S_2O_3$-solution.

The precipitate of AgI differs from the precipitates of AgCl and AgBr by its colour, and by its very slight solubility in AmOH; but it is distinguished with greater certainty by its behaviour when it is heated with strong H_2SO_4 as follows.

If the liquid is decanted from the precipitate, and the precipitate is then heated with strong H_2SO_4, the acid will be coloured red, and violet vapour of iodine will be seen on looking down the test-tube: the coloured vapour is most distinctly seen after the tube has been allowed to cool for a short time.

If a mere trace of iodine vapour is evolved, it may be detected by holding in the test-tube a glass rod which has been dipped into freshly-made starch solution (*Note* 1); the starch will be coloured blue (*Note* 2).

Note 1.—Starch solution is made by stirring a little starch powder with some water in a small porcelain dish, then boiling for a few seconds, and cooling the solution.

Note 2.—The blue colour produced by the action of iodine on starch is commonly stated to be due to the formation of a compound known as "iodide of starch."

The production of this colour requires the presence of an iodide with the starch and iodine, hence the addition of a little KI-solution to the starch-solution makes the above test for iodine vapour more delicate. But the starch solution containing iodide must not be used when substances are present which would liberate iodine from the iodide, and must not be added to a liquid where the introduction of iodide is not permissible.

553. **$CuSO_4$-solution** produces a white precipitate of cuprous iodide, Cu_2I_2, and causes the separation of iodine which colours the liquid brown:—

$$4KI + 2CuSO_4 = Cu_2I_2 + I_2 + 2K_2SO_4.$$

If the copper sulphate solution has been mixed with solution

of H_2SO_3 or $FeSO_4$ before it is added to the iodide, the precipitate and liquid are not discoloured by free iodine :—

$$2CuSO_4 + 4KI + H_2SO_3 + H_2O = Cu_2I_2 + 2K_2SO_4 + H_2SO_4 + 2HI.$$

The formation of the precipitate is accelerated by warming the liquid.

Separate this precipitate from the liquid by decantation or by filtration, and warm it with strong H_2SO_4; the acid will become red, and violet iodine vapour will be evolved which colours starch solution (552).

Solutions of chloride and of bromide differ from solution of iodide by not being precipitated by $CuSO_4$-solution.

554. **Strong H_2SO_4,** if it is warmed with a solid iodide, causes the evolution of acid fumes (HI), accompanied by violet iodine vapour. If the iodine vapour is large in quantity, it will condense on the inside of the test-tube as a black solid.

The iodine vapour colours starch-solution blue. This may be proved by holding in the vapour a glass rod, or a strip of paper, which has been moistened with freshly-made starch-solution (*Notes*, 552); or by pouring out the heavy iodine vapour into a white porcelain dish, the inside of which has been wetted with the starch-solution.

Iodine is evolved in larger quantity, if MnO_2 has been mixed with the iodide before it is warmed with H_2SO_4 (541).

555. **Chlorine-water,** or solution of bleaching-powder which has been acidified with HCl, if it is added carefully drop by drop to solution of an iodide sets iodine free. The iodine dissolves in the water colouring it brown : some of the iodine may also separate as a black powder.

The addition of Cl in excess must be carefully avoided, as it would form colourless iodine chloride, which does not give the following results.

Divide the brown liquid into three parts in three test-tubes, and proceed as follows :—

1. **Heat** one part; violet iodine vapour will be given off, and will be seen on looking down the test-tube at a white surface. The colour is most distinctly seen if some strong H_2SO_4 is added to the liquid before it is heated. If a glass rod is dipped into starch-solution (*Notes*, 552) and is then held in the iodine vapour, the starch will become blue.

2. **Starch-solution** (*Note* 1, 552), if it is added to another portion of the brown solution, produces an intense blue colour. The

colour often appears black, unless much starch-solution is added and the liquid is largely diluted. When the blue liquid is heated it becomes colourless, but it often regains its colour on being cooled: the liquid must be diluted, and the starch must be added in excess, in order to ensure the removal of the colour by heat.

3. **A drop of CS_2** is added to the third portion of the brown solution, and it is well shaken; the CS_2 will dissolve the iodine, and this solution will gradually settle down as a violet layer beneath the water, when the liquids are allowed to stand at rest.

A little KOH solution is then added, and the liquids are shaken together; the violet colour of the CS_2 will disappear, owing to the formation of the colourless salts KI and KIO_3.

556. **Nitrous acid, HNO_2.**—If a little KNO_2 is dissolved in solution, of an iodide and a dilute acid is added, HNO_2 is produced and liberates the iodine.

A solution of NO_2 in dilute H_2SO_4 (1399) also liberates iodine from an iodide.

The iodine thus liberated may be identified by the three methods described in paragraph 555; of these the starch-test and the CS_2-test are the most delicate.

When either of the two reagents mentioned above is used for liberating iodine from an iodide, it presents the advantage over Cl (555) that it does not hinder the detection of the iodine, even when it has been added in excess. These two reagents also present the advantage that they do not liberate Br from a bromide.

557. **$HgCl_2$-solution** gives with solution of an iodide a scarlet precipitate, HgI_2, which is easily soluble in excess of solution of $HgCl_2$ or of the iodide. With a solution of bromide or chloride, $HgCl_2$ gives no precipitate.

558. **$Pb\bar{A}_2$-solution** gives with solution of iodide a *bright yellow* precipitate, PbI_2: if this precipitate is dissolved in the least possible quantity of boiling water, it separates again in the form of golden yellow crystals when the liquid is cooled.

With solution of bromide or chloride, $Pb\bar{A}_2$-solution gives a *white* precipitate.

559. **Hydrogen iodide, or Hydriodic acid, HI,** is a colourless, fuming, soluble gas, resembling HCl and HBr. Its solution differs from solution of HCl or of HBr by evolving iodine when it is heated with MnO_2.

560. **Iodine** is a bluish-black solid which fuses at 114° C. and boils at 184° C., passing into purple vapour. It is soluble in water to the extent of only 0·02 per cent. forming a brown solution, but is more soluble in KI-solution, in alcohol and in other organic liquids. Its solution in most liquids is brown in colour, but the carbon disulphide and chloroform solutions are purple.

Iodine possesses only feeble oxidising power.

It is usually identified by the colour of its vapour, confirmed by the coloration of starch solution (*Notes*, 552).

DETECTION OF CHLORIDE, BROMIDE, OR IODIDE, WHEN IT OCCURS ALONE.

561. **Chloride, Bromide, or Iodide** is easily detected by the foregoing tests.

The reactions given in paragraphs 541 and 542 are perhaps the most characteristic tests for a chloride; and the tests described in paragraphs 547–549 serve to distinguish a bromide; an iodide is detected with the greatest ease and certainty by the reaction described in 556.

The colour of the precipitate which has been produced by adding $AgNO_3$ to the solution made acid with HNO_3, and the behaviour of this precipitate with AmOH, are less trustworthy indications than the above tests; but they often serve to demonstrate which of these acid-radicles is present, since AgCl is *pure white* and is very easily soluble in AmOH, AgBr is *pale yellow* and is not readily soluble in AmOH, while AgI is *primrose-yellow* and is almost insoluble in AmOH.

The action of hot strong H_2SO_4 on the precipitate of AgI, which is described in paragraph 552, is also distinctive of iodide.

DETECTION OF CHLORIDE, BROMIDE, AND IODIDE, WHEN THEY OCCUR TOGETHER.

562. The detection of these acid-radicles, when they occur together in solution, may be effected by any of the methods described in paragraphs 564, 565, 566.

If chloride is known to be absent, bromide and iodide may be rapidly tested for by the gradual addition of Cl-water in the presence of CS_2 (564), or by fractional precipitation with $AgNO_3$-solution (566).

563. **Insoluble Compounds** must be decomposed by means of Na_2CO_3, in order to obtain the chloride, bromide, and iodide in solution.

Boiling with Na_2CO_3-solution will effect this change in the case of some substances, but heating the finely-powdered substance with three times its weight of fusion mixture ($Na_2CO_3 + K_2CO_3$) on platinum foil or in a platinum capsule is a more certain and general method.

The carbonates are kept in the fused condition with the substance for about ten minutes; the mass is then allowed to cool, and is boiled with water, and the filtered solution is examined by one of the following methods (564–566).

This treatment with fused alkaline carbonates may also be employed for rendering the precipitate which has been produced by $AgNO_3$ (539, 546, 552) suitable for the following examination.

FIRST METHOD.

564. The most convenient method of examining for chloride, bromide, and iodide, when they may be present together in an aqueous solution, consists in testing for bromide and iodide in one part of the liquid by the chlorine-test (548, 555); then driving off bromine and iodine, if they are present, from another part of the liquid by means of an oxidising solution, and testing for chloride by $AgNO_3$ (539).

Note.—The aqueous solution of the substance to be tested is referred to below as the "original solution." If the substance is insoluble in water, it must be treated as is directed in paragraph 563, in order to obtain the acid-radicles in solution in water.

To a portion of the original solution, which is to be tested, add a few drops of CS_2: then add to it cautiously, drop by drop, either chlorine-water or acidified solution of bleaching-powder, and shake the liquid after each addition.

If the CS_2 does not become Coloured, bromide and iodide are absent; chloride may then be tested for, by adding to another part of the original solution HNO_3 in excess and $AgNO_3$ (539).

If the CS_2 becomes Coloured, note the colour which first appears. If the CS_2 becomes *brown* at once, bromide is present and iodide is absent; if the CS_2 is coloured *violet* iodide is present, and the cautious addition of the chlorine solution must be continued, constantly shaking the liquid and watching whether, as the violet colour disappears a brown colour takes its place; if the CS_2 turns *brown,* the presence of bromide is proved: if no brown colour appears, bromide is absent.

Proceed to test for chloride as is directed below.

Remove bromine and iodine from another portion of the original solution by acidifying with dilute H_2SO_4, adding a little potassium permanganate solution (see *Note*), and boiling the solution in a porcelain dish until the brown colour of the liquid disappears. Then add more permanganate solution cautiously and boil the liquid, and continue these processes until the addition of permanganate no longer produces any brown colour, and the liquid retains a pale pink colour for a few seconds: this proves that all bromide and iodide have been removed.

Now add $AgNO_3$: the formation of a white precipitate will prove the presence of chloride.

Note.—Instead of permanganate one of the following oxidising solutions may be used. (1) Dilute HNO_3, prepared by mixing one volume of acid (1·42 sp. gr.) with three volumes of water; or (2) *cold* solution of ammonium persulphate. This must be added in successive quantities, and the liquid must be heated for a time after each addition, until a brown coloration of

the solution is no longer seen. The bromine and iodine will then have been completely removed.

SECOND METHOD.

565. After testing for iodide and bromide by repeatedly shaking part of the original solution (*Note*, 564) with CS_2 during the gradual addition of Cl-water, or of acidified $CaCl_2O$-solution (564), the presence of chloride may be detected, and the presence of iodide and bromide confirmed by successive fractional precipitation with $AgNO_3$-solution.

For this purpose the rest of the original solution is mixed with $AgNO_3$-solution (1 : 100), added drop by drop: yellow AgI will first be formed, and may be removed by shaking or boiling the liquid and filtering off the coagulated AgI: when the yellow AgI is no longer produced and removed, pale-yellow AgBr will appear; and after this has been removed in a similar manner, pure white AgCl will be precipitated. The colour of the silver salt is most easily judged by contrast with white filter-paper.

THIRD METHOD.

566. This method of examination is varied according as iodide is present or absent. Since chloride cannot be detected in the presence of iodide, the iodide must be separated before proceeding to examine for the chloride.

To a small portion of the Original Solution (*Note*, 564), which has been made just acid by the addition of dilute H_2SO_4, add a little cold freshly-prepared starch-solution (*Note* 1, 552). Then add, drop by drop, either strong HNO_3, or solution of nitrous acid (556): the appearance of a dark blue coloration will show the **Presence of Iodide.**

Examine the remainder of the original solution for chloride and bromide, according to the directions given under (**a**) or (**b**), the selection of the method depending upon whether iodide has been found or not.

(**a**) **Iodide is Present.**—Add to the original solution a mixture of $CuSO_4$-solution with half its measure of strong H_2SO_3-solution, and warm gently for a short time: Cu_2I_2 will be precipitated (553).

In order to ascertain whether the iodide has been entirely precipitated, filter a small quantity of the liquid and warm it with a little more of the above reagent. If any further precipitate is produced, return the filtered portion to the unfiltered liquid. Then add more of the reagent to the whole of the liquid, warm it again for a time and test it again, in order to see if the removal of iodide is complete. Repeat these trials until a small portion of the filtrate gives no further precipitate, when it is warmed with more of the reagent.

Then filter, repeating the filtration if necessary, until the liquid is perfectly clear, add KOH in excess to the filtrate, and boil the liquid. Filter off the precipitate thus produced; and test the filtrate, which is now free from iodide, for bromide and chloride as is directed below (**b**).

(**b**) **Iodide is Absent.**—Make the solution alkaline, if it is not already so, by the addition of pure KOH, and evaporate it to dryness in a porcelain dish. Scrape the residue off the sides of the dish, and mix it with three or four times as much powdered $K_2Cr_2O_7$ by rubbing the two substances together in the dish with a pestle.

Transfer this mixture to the tube or flask shown in Fig. 56, p. 135 or to a Clarke's retort (Fig. 57, p. 147), taking the greatest care to let none of the powder remain in the neck or in the delivery-tube.

Then pour in sufficient strong H_2SO_4 to cover the powder to the depth of about a quarter of an inch, and mix the acid and powder by cautious shaking.

Dip the end of the delivery-tube into water contained in a test-tube or receiver and warm the mixture gently, carefully guarding against any of the mixture passing over into the water in the test-tube or receiver.

As soon as no more reddish-brown vapour is visible in the delivery-tube discontinue the heating, and immediately withdraw the tube containing the water.

If no coloured vapour has been evolved and the water in the tube is colourless, chloride and bromide are absent.

If the water is coloured, pour into it sufficient CS_2 to form a layer about half an inch in depth at the bottom of the test-tube. Close the mouth of the tube with the thumb, shake the tube vigorously, and then allow it to stand at rest. If the CS_2, as it settles down, shows a brown colour, this indicates **the Presence of Br,** derived from bromide.

Separate the water from the CS_2 by pouring it through a wet filter; add to the filtrate AmOH in excess, then $H\bar{A}$ in excess and then $Pb\bar{A}_2$-solution. The formation of a yellow precipitate indicates the presence of chromate, and this proves indirectly that **Chloride was present** (542) in the original substance.

GROUP V.—PHOSPHATE GROUP.

567. This Group includes phosphate, arsenate, phosphite and hypophosphite; the two former are important and resemble one another closely in their reactions.

PHOSPHORIC ACID AND THE PHOSPHATES.

568. Phosphoric oxide, P_2O_5, unites with water in different proportions to form three phosphoric acids, orthophosphoric acid H_3PO_4, pyrophosphoric acid $H_4P_2O_7$, and metaphosphoric acid HPO_3. When orthophosphoric acid is heated to 250° C. water is given off and pyrophosphoric acid remains; and when either of these acids is heated to redness more water is eliminated and metaphosphoric acid remains.

Where either the pyro- or meta-acid is dissolved in water it recombines with water and forms orthophosphoric acid; this takes place slowly in the cold, but rapidly when the water is heated.

In the ordinary course of analysis pyrophosphate and metaphosphate, if they were originally present, have been converted by solution in water into orthophosphate, hence they must be sought for by special methods applied to the original substance.

ORTHOPHOSPHATE, $(PO_4)'''$.—Use Sodium hydrogen phosphate, $Na_2HPO_4.12H_2O$.

569. **$MgSO_4$-solution,** to which some AmCl has been added and then a little AmOH, gives with solution of phosphate a white crystalline precipitate, $MgAmPO_4.6H_2O$.

This precipitate is almost insoluble in AmOH, but is easily soluble in acids. If very little phosphate is present, the precipitate often appears only when the liquid has been gently warmed, then well stirred or shaken, and then allowed to stand for some time.

570. **$FeCl_3$-solution,** if it is dropped into phosphate solution, to which a little $H\bar{A}$ and $Na\bar{A}$-solution have been previously added, gives a yellowish-white precipitate, $FePO_4$.

571. **Ammonium molybdate, $AmHMoO_4$.**—When a drop of phosphate-solution is added to a solution of Am_2MoO_4 in HNO_3, which is assumed to contain $AmHMoO_4$, a yellow precipitate is produced *in the cold.* (Difference from pyro- and metaphosphate.)

The formation of this precipitate is hastened by gently warming and stirring or shaking the liquid; but the precipitate appears only after a time in very dilute solution of a phosphate. (See *Precautions.*)

A part of the precipitate usually adheres firmly to the inside of the tube; this may be removed by solution of KOH, NaOH, or AmOH, in which it is readily soluble. The precipitate is only slightly soluble in inorganic acids, and is practically insoluble in HNO_3.

Precautions.—This is a most delicate test if it is properly performed. It serves to detect the presence of a mere trace of phosphate, when careful attention is paid to the following precautions.

The $AmHMoO_4$-solution must be prepared according to the directions given in paragraph 1410, Remark 10.

The solution to be tested must not be alkaline to test-paper. It should be made distinctly acid by addition of HNO_3, and then added *in small quantity only* to some of the $AmHMoO_4$-solution in a test-tube. More of the test-solution must only be added if no yellow precipitate forms after the mixed solutions have been gently warmed and stirred.

This last precaution is extremely important, since the presence of *an excess of phosphate altogether prevents the formation of the precipitate.*

Show that this is the case, by pouring a few drops of $AmHMoO_4$-solution into some Na_2HPO_4-solution which has been acidified with HNO_3. No precipitate will form even when the liquid is heated and shaken, since the phosphate is present in large quantity in relation to the $AmHMoO_4$. If a few drops of this liquid mixture, however, are now added to some fresh $AmHMoO_4$-solution, the precipitate will appear.

It must also be remembered that the presence of much HCl retards or prevents the formation of this precipitate. A solution of the test-substance, acidified with nitric acid alone, should therefore be used if possible.

Dip the end of the delivery-tube into water contained in a test-tube or receiver and warm the mixture gently, carefully guarding against any of the mixture passing over into the water in the test-tube or receiver.

As soon as no more reddish-brown vapour is visible in the delivery-tube discontinue the heating, and immediately withdraw the tube containing the water.

If no coloured vapour has been evolved and the water in the tube is colourless, chloride and bromide are absent.

If the water is coloured, pour into it sufficient CS_2 to form a layer about half an inch in depth at the bottom of the test-tube. Close the mouth of the tube with the thumb, shake the tube vigorously, and then allow it to stand at rest. If the CS_2, as it settles down, shows a brown colour, this indicates **the Presence of Br,** derived from bromide.

Separate the water from the CS_2 by pouring it through a wet filter; add to the filtrate AmOH in excess, then $H\bar{A}$ in excess and then $Pb\bar{A}_2$-solution. The formation of a yellow precipitate indicates the presence of chromate, and this proves indirectly that **Chloride was present** (542) in the original substance.

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Where either the pyro- or meta-acid is dissolved in water it recombines with water and forms orthophosphoric acid; this takes place slowly in the cold, but rapidly when the water is heated.

In the ordinary course of analysis pyrophosphate and metaphosphate, if they were originally present, have been converted by solution in water into orthophosphate, hence they must be sought for by special methods applied to the original substance.

ORTHOPHOSPHATE, $(PO_4)'''$.—Use Sodium hydrogen phosphate, $Na_2HPO_4.12H_2O$.

569. **$MgSO_4$-solution,** to which some AmCl has been added and then a little AmOH, gives with solution of phosphate a white crystalline precipitate, $MgAmPO_4.6H_2O$.

This precipitate is almost insoluble in AmOH, but is easily soluble in acids. If very little phosphate is present, the precipitate often appears only when the liquid has been gently warmed, then well stirred or shaken, and then allowed to stand for some time.

570. **$FeCl_3$-solution,** if it is dropped into phosphate solution, to which a little $H\bar{A}$ and $Na\bar{A}$-solution have been previously added, gives a yellowish-white precipitate, $FePO_4$.

571. **Ammonium molybdate, $AmHMoO_4$.**—When a drop of phosphate-solution is added to a solution of Am_2MoO_4 in HNO_3, which is assumed to contain $AmHMoO_4$, a yellow precipitate is produced *in the cold.* (Difference from pyro- and metaphosphate.)

The formation of this precipitate is hastened by gently warming and stirring or shaking the liquid; but the precipitate appears only after a time in very dilute solution of a phosphate. (See *Precautions.*)

A part of the precipitate usually adheres firmly to the inside of the tube; this may be removed by solution of KOH, NaOH, or AmOH, in which it is readily soluble. The precipitate is only slightly soluble in inorganic acids, and is practically insoluble in HNO_3.

Precautions.—This is a most delicate test if it is properly performed. It serves to detect the presence of a mere trace of phosphate, when careful attention is paid to the following precautions.

The $AmHMoO_4$-solution must be prepared according to the directions given in paragraph 1410, Remark 10.

The solution to be tested must not be alkaline to test-paper. It should be made distinctly acid by addition of HNO_3, and then added *in small quantity only* to some of the $AmHMoO_4$-solution in a test-tube. More of the test-solution must only be added if no yellow precipitate forms after the mixed solutions have been gently warmed and stirred.

This last precaution is extremely important, since the presence of *an excess of phosphate altogether prevents the formation of the precipitate.*

Show that this is the case, by pouring a few drops of $AmHMoO_4$-solution into some Na_2HPO_4-solution which has been acidified with HNO_3. No precipitate will form even when the liquid is heated and shaken, since the phosphate is present in large quantity in relation to the $AmHMoO_4$. If a few drops of this liquid mixture, however, are now added to some fresh $AmHMoO_4$-solution, the precipitate will appear.

It must also be remembered that the presence of much HCl retards or prevents the formation of this precipitate. A solution of the test-substance, acidified with nitric acid alone, should therefore be used if possible.

572. **$AgNO_3$** : yellow precipitate, Ag_3PO_4 : pour off a portion of the liquid with the precipitate and show that the precipitate is soluble in AmOH and in HNO_3.

573. **Phosphine test.**—A very delicate test for the presence of P, occurring in the form of phosphate or otherwise, consists in strongly heating the dry solid substance with Mg-powder, or with a small piece of Na, in a little tube of hard glass closed at one end.

When the cool tube is broken and the powdered substance is breathed upon, an onion-like smell will be perceived; this is due to the production and escape of PH_3, which has been formed by the action of the moisture of the breath upon the metallic phosphide.

574. **Flame-coloration.**—If a phosphate is made into a paste with strong H_2SO_4, and the mixture is then strongly heated at the tip of the inner blowpipe-flame, it gives a *bluish-green* colour to the flame.

575. **Blowpipe-test.**—Many phosphates, when they are moistened on charcoal with cobalt nitrate solution, and are then heated in the outer blowpipe-flame, become *blue*.

576. **Hydrogen orthophosphate, or Orthophosphoric acid, H_3PO_4,** is a colourless crystalline substance. Its solution is strongly acid, and differs from H_2SO_4 by not charring paper which has been dipped into it and then dried by heat. The free acid does not coagulate albumin. The presence of H_3PO_4 may be detected by reactions 569, 571.

PYROPHOSPHATE, $(P_2O_7)^{IV}$.—Use Sodium pyrophosphate, $Na_4P_2O_7$.

577. Sodium pyrophosphate is made by heating solid sodium orthophosphate, Na_2HPO_4, to redness on platinum-foil or porcelain until water is no longer driven of :—$2Na_2HPO_4 = Na_4P_2O_7 + H_2O$. The cold residue is then dissolved in *cold water*, since the solution of pyrophosphate is gradually converted by heat into orthophosphate, and the solution is used at once for the following reactions.

578. **$AgNO_3$** : heavy white precipitate of silver pyrophosphate, readily soluble in AmOH and in HNO_3. (Difference from orthophosphate.)

579. **$AmHMoO_4$** produces no precipitate in the cold; but the pyrophosphate is converted into the orthophosphate when the liquid is heated, and yellow ammonium phosphomolybdate is precipitated (571).

580. **$MgSO_4$**; white precipitate, soluble in excess of either solution; but when the mixture is boiled, a precipitate is formed which does not disappear on cooling. (Difference from metaphosphate.)

581. **Albumin-solution** is not coagulated by free pyrophosphoric acid. (Difference from metaphosphoric acid.)

METAPHOSPHATE, $(PO_3)'$.—Use Sodium metaphosphate, $NaPO_3$.

582. Sodium metaphosphate is obtained by heating either microcosmic salt or NaH_2PO_4 to redness on platinum foil or porcelain :—$NaNH_4HPO_4 = NaPO_3 + NH_3 + H_2O$. The cold residue is dissolved in *cold water* since,

like pyrophosphate, metaphosphate is slowly converted into orthophosphate when its solution is heated: this solution is used at once for the following reactions.

583. **$AgNO_3$** : white flocculent precipitate of silver metaphosphate, soluble in AmOH and in HNO_3.

584. **$MgSO_4$** : no precipitate from moderately dilute solution of metaphosphate even on boiling the liquid. (Difference from ortho- and pyrophosphates.)

585. **$AmHMoO_4$** : no precipitate in the cold, but when the mixture is boiled yellow ammonium phospho-molybdate is precipitated (571, 579).

586. **Albumin-solution** is coagulated by metaphosphoric acid. Prove this by acidifying the metaphosphate-solution with $H\bar{A}$ in order to form metaphosphoric acid, and adding this solution to white of egg dissolved in water, the liquid will become white and semi-opaque. (Difference from ortho- and pyrophosphoric acids.)

ARSENATE, $(AsO_4)'''$.—Use $Na_2HAsO_4.12H_2O$ solution.

587. The precipitates formed in reactions 569–571 by a phosphate are precisely similar in appearance and general properties to those formed by the same reagents with solution of an arsenate; but $AmHMoO_4$ gives a precipitate with an arsenate *only when the liquid is boiled*, and not when it is *gently heated*, as in the case of a phosphate.

The precipitate (Ag_3AsO_4) which $AgNO_3$ gives with an arsenate is *brown*, while that given by a phosphate is *yellow* (572).

DETECTION AND SEPARATION OF PHOSPHATE, ARSENATE AND ARSENITE.

588. **The following Differences** serve to detect and separate phosphate and arsenate:—

1. The fact that an arsenate yields a precipitate with $AmHMoO_4$ only when the liquid is *boiled*, whereas the corresponding precipitate is produced by a phosphate when the liquid is only *gently heated*.

2. Arsenate solution, which has been boiled with strong HCl, gives, when H_2S is passed into the hot liquid, first a white precipitate of S and then yellow As_2S_3; phosphate solution under the same circumstances gives no precipitate.

3. In *perfectly neutral* arsenate solution $AgNO_3$ gives a *brown* precipitate; in neutral phosphate solution it gives a *canary yellow* precipitate.

DETECTION OF PHOSPHATE OR ARSENATE.

589. **The Simplest Method of ascertaining which of these two Acid-radicles is present** is to throw the precipitate, which has been produced by the addition of AmCl, AmOH and $MgSO_4$ (569) upon a filter; then wash it with a little cold water, and drop $AgNO_3$-solution upon it. If the precipitate consists of $MgAmAsO_4$, it will become *brown*; if it is $MgAmPO_4$, it will become *canary-yellow*.

The precipitate, which has been produced by the addition of AmCl, AmOH and $MgSO_4$, may also be examined for arsenate by dissolving part of it in dilute HNO_3, adding $AgNO_3$-solution as long as it causes any white precipitate, and then adding *very dilute* AmOH gradually drop by drop.

If arsenate is present, a *brown* precipitate will form just before the liquid becomes alkaline to test-paper: a phosphate will give a *yellow* precipitate.

Instead of mixing the dilute AmOH with the acid liquid, the AmOH may be gently poured in upon the top of the liquid: the colour will then appear at the surface of contact of the ammonia solution with the acid liquid.

DETECTION OF ARSENATE, PHOSPHATE AND ARSENITE, WHEN THEY ARE PRESENT TOGETHER.

590. A clear mixture of solutions of $MgSO_4$, AmCl and AmOH is added as long as it causes any further precipitate, the liquid is filtered and the filtrate is preserved.

A small portion of the precipitate is then tested at once for arsenate by dropping $AgNO_3$-solution upon it. If the precipitate turns yellow, *Phosphate is present, and Arsenate is absent.* If the precipitate turns brown, *Arsenate is present*, and phosphate may also be present.

The arsenate must be separated from the other part of the precipitate before phosphate can be tested for.

The rest of the precipitate is accordingly dissolved in a little boiling strong HCl, and H_2S is passed for several minutes into this hot solution; the presence of an arsenate will be confirmed by the liquid becoming milky owing to the separation of white S, which is followed by the precipitation of yellow As_2S_3 (174).

This precipitate is filtered off and H_2S is again passed into the boiling filtrate. If any further precipitate is produced, the gas must be further passed until it no longer causes a precipitate in the boiling liquid.

The precipitation by H_2S is rendered complete without delay, if the original solution in HCl is first treated with H_2SO_3. See paragraph 174.

The liquid is then filtered and the clear filtrate is evaporated just to dryness, the residue is dissolved in a little dilute HNO_3, and this solution is tested for phosphate by adding a few drops of it to $AmHMoO_4$-solution and gently warming the liquid : a yellow precipitate will indicate the **presence of Phosphate** (571).

Arsenite may be tested for by acidifying the filtrate, which has been reserved from the original Mg-precipitate, and passing H_2S into it : yellow As_2S_3 will be precipitated *at once* if arsenite is present.

PHOSPHITE, $(PHO_3)''$.—Use solution of Na_2PHO_3.

591. **$AgNO_3$** : black precipitate, Ag, when the liquid is allowed to stand or is heated. The addition of AmOH in small quantity increases the delicacy of this test, but it must be remembered that the original precipitate is soluble in excess of this reagent.

592. **$HgCl_2$** : white precipitate, Hg_2Cl_2, which becomes grey, Hg, when the liquid in which it is suspended is heated.

593. **$Pb\bar{A}_2$**: white precipitate, $PbPHO_3$, which is insoluble in acetic acid.

594. **$BaCl_2$** : white amorphous precipitate, soluble in all acids.

595. **Reduction reactions.**—Solution of phosphorous acid, or of a phosphite which has been acidified with $H\bar{A}$, acts as a reducing agent : but its action is not as powerful as that of hypophosphorous acid (601), as the following reactions will show :—

(*a*) A drop of **$KMnO_4$**–solution is not reduced and decolorised by phosphorous acid : but reduction, attended with loss of colour, takes place when the liquid is heated.

(*b*) A drop of **$CuCl_2$**– or of **$CuSO_4$**–solution is not reduced and decolorised even when the liquid is heated more strongly.

596. **Solid Phosphite,** when it is heated, gives off a mixture of hydrogen and hydrogen phosphide : the latter gas is known by its garlic smell : the mixture of gases is spontaneously inflammable in contact with air, and burns with a bright white flame emitting white fumes : red phosphorus is usually deposited in the ignition-tube and sodium phosphate remains.

HYPOPHOSPHITE, $(PH_2O_2)'$.—Use solution of $NaPH_2O_2$.

597. **$AgNO_3$** : white precipitate, $AgPH_2O_2$, which gradually becomes black ; the change is more rapid when the liquid is heated, and is due to the formation of metallic silver.

598. **$HgCl_2$** : white precipitate, Hg_2Cl_2, which forms slowly on standing, but more rapidly when the liquid is heated.

599. **$Pb\bar{A}_2$** : no precipitate. (Difference from phosphite.)

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The precipitate, which has been produced by the addition of AmCl, AmOH and $MgSO_4$, may also be examined for arsenate by dissolving part of it in dilute HNO_3, adding $AgNO_3$-solution as long as it causes any white precipitate, and then adding *very dilute* AmOH gradually drop by drop.

If arsenate is present, a *brown* precipitate will form just before the liquid becomes alkaline to test-paper: a phosphate will give a *yellow* precipitate.

Instead of mixing the dilute AmOH with the acid liquid, the AmOH may be gently poured in upon the top of the liquid: the colour will then appear at the surface of contact of the ammonia solution with the acid liquid.

DETECTION OF ARSENATE, PHOSPHATE AND ARSENITE, WHEN THEY ARE PRESENT TOGETHER.

590. A clear mixture of solutions of $MgSO_4$, AmCl and AmOH is added as long as it causes any further precipitate, the liquid is filtered and the filtrate is preserved.

A small portion of the precipitate is then tested at once for arsenate by dropping $AgNO_3$-solution upon it. If the precipitate turns yellow, *Phosphate is present, and Arsenate is absent.* If the precipitate turns brown, *Arsenate is present,* and phosphate may also be present.

The arsenate must be separated from the other part of the precipitate before phosphate can be tested for.

The rest of the precipitate is accordingly dissolved in a little boiling strong HCl, and H_2S is passed for several minutes into this hot solution; the presence of an arsenate will be confirmed by the liquid becoming milky owing to the separation of white S, which is followed by the precipitation of yellow As_2S_3 (174).

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The liquid is then filtered and the clear filtrate is evaporated just to dryness, the residue is dissolved in a little dilute HNO_3, and this solution is tested for phosphate by adding a few drops of it to $AmHMoO_4$-solution and gently warming the liquid : a yellow precipitate will indicate the **presence of Phosphate** (571).

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PHOSPHITE, $(PHO_3)''$.—Use solution of Na_2PHO_3.

591. **$AgNO_3$** : black precipitate, Ag, when the liquid is allowed to stand or is heated. The addition of AmOH in small quantity increases the delicacy of this test, but it must be remembered that the original precipitate is soluble in excess of this reagent.

592. **$HgCl_2$** : white precipitate, Hg_2Cl_2, which becomes grey, Hg, when the liquid in which it is suspended is heated.

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(*a*) A drop of **$KMnO_4$**-solution is not reduced and decolorised by phosphorous acid : but reduction, attended with loss of colour, takes place when the liquid is heated.

(*b*) A drop of **$CuCl_2$**– or of **$CuSO_4$**–solution is not reduced and decolorised even when the liquid is heated more strongly.

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HYPOPHOSPHITE, $(PH_2O_2)'$.—Use solution of $NaPH_2O_2$.

597. **$AgNO_3$** : white precipitate, $AgPH_2O_2$, which gradually becomes black ; the change is more rapid when the liquid is heated, and is due to the formation of metallic silver.

598. **$HgCl_2$** : white precipitate, Hg_2Cl_2, which forms slowly on standing, but more rapidly when the liquid is heated.

599. **$Pb\bar{A}_2$** : no precipitate. (Difference from phosphite.)

600. **$BaCl_2$** : no precipitate. (Difference from phosphite.)

601. **Reduction reactions.**—Solution of hypophosphorous acid, or of a hypophosphite which has been acidified with HĀ, acts as a powerful reducing reagent: this is proved by the following reactions :—

(*a*) A drop of **$KMnO_4$**-solution is reduced and decolorised, when it is added to the cold solution.

(*b*) When the solution is mixed with a little **$CuSO_4$**-solution and the mixture is heated to 55° C., red copper hydride, CuH_2, is precipitated, and this evolves H and leaves metallic copper when the liquid is heated more strongly.

(*c*) When the solution is mixed with a little **$CuCl_2$**-solution, the copper salt is decolorised and white Cu_2Cl_2 is precipitated; the Cu_2Cl_2 then gradually changes to red metallic copper.

602. **Solid Hypophosphite,** when it is heated, gives off hydrogen phosphide; this gas may be recognised by its garlic smell, and by kindling spontaneously in contact with the air: it burns with a bright white flame which emits white fumes and usually deposits red phosphorus on the interior of the ignition tube. The residue in the tube consists of sodium phosphate.

GROUP VI.—PER-SALT GROUP.

603. This Group includes permanganate and the related manganate, persulphate, perchlorate and periodate; also percarbonate and perborate, which are unstable and of less importance.

Hydrogen peroxide, H_2O_2, and ozone are also included in this group.

The above grouping is somewhat indefinite, since it associates the salts of the higher acids, $HMnO_4$, $HClO_4$, HIO_4 and the salts of the true per-acids $H_2S_2O_8$, $H_2C_2O_6$ and HBO_4. Many of the rarer per-acids and their salts are not described here.

PERMANGANATE, $(MnO_4)'$.—Use solution of $KMnO_4$.

Solid permanganates are usually very dark red or purple in colour; their solutions are usually purple or reddish-purple.

604. **KOH,** if it is added in large excess, causes the purple colour of the solution to change to green: this is due to the conversion of the permanganate into manganate :—

$$2KMnO_4 + 2KHO = 2K_2MnO_4 + H_2O + O.$$

The purple colour reappears when this alkaline green liquid is acidified (610).

605. **H_2O_2**, when it is added to a permanganate solution which has been acidified with H_2SO_4, reduces the permanganate to a manganese salt with evolution of oxygen :—

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = 2MnSO_4 + K_2SO_4 + 8H_2O.$$

606. **Reducing reagents.**—The addition of SO_2, H_2S, acidified solution of nitrite, or of other reducing reagents, at once destroys the purple colour of permanganate solution, and a nearly colourless manganese salt is formed. It follows that in the ordinary course of analysis permanganate will be converted into a manganous salt, which will be detected in Group III.B.

607. **Heated with Acid.**—Solid permanganate, or its strong solution, gives off oxygen when it is heated with dilute H_2SO_4, and chlorine gas when it is heated with HCl : the purple colour of the permanganate at the same time disappears. If the sulphuric acid is strong, purple vapour of Mn_2O_7 is evolved, which causes explosion since it is very unstable.

MANGANATE, $(MnO_4)''$.—Use alkaline solution of K_2MnO_4.

608. Solid manganates are almost black : their solutions are bluish-green in colour.

609. **H_2O.**—Manganates undergo decomposition in contact with water, with production of purple permanganate and MnO_2, unless much alkaline hydroxide is present :—

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + 4KOH + MnO_2.$$

610. **Acid,** if it is added in sufficient quantity, causes the green solution of manganate to change to reddish-purple solution of permanganate : even carbon dioxide produces this change, and it may therefore be brought about by exposure of the manganate solution to the air :—

$$3K_2MnO_4 + 3H_2SO_4 = 2KMnO_4 + 2K_2SO_4 + MnSO_4 + 3H_2O + O.$$

The above change is reversed when solution of an alkaline hydroxide is added in excess to the red solution (604).

611. **Reducing reagents** decolorise an acidified solution of manganate and produce manganous salt (606).

PERSULPHATE, $(S_2O_8)''$.—Use Ammonium persulphate, $Am_2S_2O_8$, dissolved in *cold* water.

612. When a **strong cold solution** is boiled, it gives off oxygen which may be collected and identified by causing a glowing wooden

splinter to burst into flame : the persulphate is meanwhile reduced to sulphate which remains in solution.

613. **$BaCl_2$** gives a precipitate only when the solution is boiled. Since, however, persulphate almost invariably contains sulphate as a product of decomposition, the test should be made by adding $BaCl_2$ in excess, filtering off any $BaSO_4$ through a double filter paper, and then boiling the clear filtrate : the formation of a white precipitate by boiling indicates the presence of persulphate.

614. **Mn- or Pb-salts** give a brown precipitate of the corresponding hydrated peroxide when the liquid is boiled : Ni- and Co-salts give a similar result in alkaline solution of persulphate.

615. **$KMnO_4$**, in acidified solution, is not decolorised by persulphate. (Difference from H_2O_2).

PERCHLORATE, $(ClO_4)'$.—Use $KClO_4$ solution.

616. The perchlorates are more stable than the chlorates. An aqueous solution of perchloric acid is stable and may be preserved indefinitely even when exposed to the light, if it does not contain more than 71 per cent. of the acid. All perchlorates are soluble in water.

617. **Action of acids.**—Perchlorate is not decomposed when it is boiled with HCl. (Difference from chlorate.)

H_2SO_4 has no action on perchlorate in the cold, but the hot strong acid forms $HClO_4$ which may be distilled if proper precautions are observed.

618. **Potassium salts** precipitate from $HClO_4$-solution the relatively insoluble, white, crystalline $KClO_4$; alcohol causes the precipitation to be complete.

619. **H_2SO_3-solution** does not reduce perchlorate (519). (Difference from chlorate.)

620. **Dry reactions.**—Perchlorates require a higher temperature than chlorates for their decomposition by heat, but they deflagrate when they are heated on charcoal in the blowpipe-flame (522).

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621. **Periodate, Periodic acid.**—Periodic acid, HIO_4, is unknown ; but para-periodic acid has been prepared. It has the formula $HIO_4.2H_2O$, or H_5IO_6, and forms deliquescent crystals which fuse at 133° C. and decompose at 150° C. into I_2O_5, H_2O and O.

Sodium periodate, $Na_2H_3IO_6$, and many complex periodates are also known.

Periodic acid and its salts are more stable than the corresponding chlorine compounds.

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622. **Percarbonate.**—Free percarbonic acid is unknown, but its potassium salt ($K_2C_2O_6$), which is pale blue in colour, is stable in the dry state.

Moisture decomposes this salt into $KHCO_3$ and H_2O_2. Cold dilute H_2SO decomposes it with evolution of CO_2 and formation of $KHSO_4$ and H_2O_{24}.

The salt therefore acts as an oxidising agent like H_2O_2, and gives all the characteristic reactions of this substance.

Percarbonate may be distinguished from H_2O_2 by adding it in small quantity and in a powdered condition to excess of KI-solution ; if $K_2C_2O_6$ is present, I will be set free at once :—$K_2C_2O_6 + 2KI = 2K_2CO_3 + I_2$; if only $KHCO_3$ and H_2O_2 are present the I is liberated much more slowly.

$AgNO_3$ and $BaCl_2$-solutions give with percarbonate white precipitates which are soluble in dilute HNO_3.

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623. **Perborate.**—Sodium perborate, $NaBO_3.4H_2O$, is a white crystalline salt, which is stable in the air. Its aqueous solution is alkaline and contains H_2O_2 : the solution decomposes when it is heated above 40° C. and oxygen is evolved.

Perborate solution liberates I from KI-solution, and oxidises solution of ferrous salt to ferric salt, chromic acid to perchromic acid, and manganous salt to manganese dioxide.

When perborate solution is added to dilute H_2SO_4 containing 50 per cent. of acid, H_3BO_3 is precipitated and H_2O_2 remains in solution.

Sodium perborate solution may be shown to bleach blue litmus readily, and its main industrial application is for bleaching.

HYDROGEN PEROXIDE, H_2O_2.—Use a 3 per cent., or 10-volume, solution of H_2O_2.

624. A little H_2O_2-solution may be prepared by adding a small quantity of sodium peroxide to *ice-cold* water ; this will produce a clear strongly alkaline solution which gives all the reactions of H_2O_2. When this solution is to be used for the "acid reactions" described below it must be acidified with dilute H_2SO_4, carefully keeping the liquid cool during the addition of the acid.

625. **Titanium sulphate, $Ti(SO_4)_2$,** gives to acid H_2O_2-solution a distinct yellow colour, which is due to the formation of pertitanic acid :—$TiO_2 + H_2O_2 = TiO_3 + H_2O$. On the addition of an alkali a yellowish orange precipitate is formed which dissolves in excess of the reagent. This is the most delicate test for H_2O_2. (Difference from persulphate.)

626. **Chromic acid.**—Add to an acid solution of the peroxide a little ether free from alcohol, and a few drops of $K_2Cr_2O_7$-solution, and shake the liquids ; the upper ethereal layer will be coloured *blue* by the formation of perchromic acid. (Difference from persulphate.)

627. **Reducing action.**—$KMnO_4$ in acid solution is at once decolorised by H_2O_2 with the evolution of oxygen :—

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

Many oxides, such as Ag_2O, PbO_2, MnO_2, Co_2O_3, are reduced by H_2O_2 with evolution of oxygen in a similar way. (Difference from persulphate.)

628. Potassium iodide and Starch: if a little starch-paste containing KI-solution (552, *Notes* 1, 2) is added to the *acidified* H_2O_2 solution; a blue colour will appear at once:—$2KI + H_2O_2 = 2KOH + I_2$.

629. $AuCl_3$ is reduced by alkaline H_2O_2-solution with separation of the metal and evolution of oxygen. The gold separates in a very finely divided state, and appears brown by reflected light and blue by transmitted light.

630. Mn- or Co-salt in solution gives a dark coloured precipitate of the hydrated peroxide of the metal. Hypochlorite solution gives the same reaction with Mn- or Co-salt, but it does not reduce gold chloride solution (629).

OZONE, O_3.

631. Ozone is always formed where oxygen is exposed to the silent electric discharge. It is also formed to some extent in many reactions which liberate oxygen, as when BaO_2, MnO_2 or $KMnO_4$ is mixed with sulphuric acid. Ozone is also formed during the slow oxidation of many substances in the air, notably by the oxidation of ordinary phosphorus. It is a strong oxidising agent and behaves like H_2O_2 in many respects.

DIFFERENCE BETWEEN HYDROGEN PEROXIDE (H_2O_2) and OZONE (O_3) IN THEIR REACTIONS.

632. Ozone and hydrogen peroxide may be distinguished by the following reactions.

(*a*) Iodine is set free immediately by ozone from dilute *neutral* potassium iodide solution: H_2O_2 requires the presence of free acid for the liberation of I (628).

(*b*) Bromine is liberated by ozone from an acid solution of sodium bromide: this effect is not produced by H_2O_2.

(*c*) A strip of silver-foil which has been polished with emery-paper and then heated for a moment in the Bunsen-flame is blackened when it is brought into contact with ozone, but not by contact with H_2O_2.

(*d*) No yellow colour is produced by ozone in titanium sulphate solution, but this colour is produced by H_2O_2 (625).

(*e*) Gold is not precipitated from its solution by ozone, but it is precipitated by H_2O_2(629).

VII.—UNGROUPED ACID-RADICLES.

633. The following Acid-radicles are not included in any of the preceding Groups :—Borate, Chromate, Silicate, Fluoride, together with the rarer Acid-radicles, Tungstate, Molybdate, Selenite, Tellurate, Tellurite, Titanate and Vanadate.

The four Acid-radicles first mentioned present no marked resemblances to one another or to other Acid-radicles in their reactions ; they are therefore usually detected by special tests.

The reactions of the rarer acid-radicles have been already described under the metals, since they are precipitated by Group-reagents for the metals.

BORATE, $(BO_3)'''$.—Use Sodium pyroborate, or Borax, $Na_2B_4O_7.10H_2O$.

634. **Turmeric-test.**—Powder some borate finely, and stir it with a little dilute HCl on a watch-glass. Immerse in this liquid one-half of a strip of turmeric-paper, and dry the strip on a watch-glass in the steam-oven (48), upon a water-bath (38), or above a small flame.

The part of the test-paper which was moistened will now appear *reddish-brown*, and will become *bluish-black* when it is moistened with AmOH.

635. **Alcohol-flame Coloration.**—Pour alcohol upon some finely-powdered borate in a porcelain dish, add a little strong H_2SO_4, then heat the mixture and kindle the vapour of the spirit.

The flame will show a *green* border, which is due to the formation and combustion of ethyl borate ; the colour of the flame is often more distinctly seen when the vapour is relighted after the flame has burnt for a time and has then been extinguished.

This flame-coloration is similar to that which is given by certain other substances ; but its spectrum, consisting of four equidistant green lines, is quite characteristic (Fig. 51, p. 50).

636. **Blowpipe-flame Coloration.**—If a mixture containing CaF_2, $KHSO_4$ and a borate is finely powdered, then moistened and heated on a loop of platinum wire in the inner blowpipe-flame for a short time, it will colour the outer flame momentarily *green.*

This test is not always decisive, since many phosphates and copper salts give a similar result.

The flame-coloration is also liable to be masked by the colorations of other substances ; but even when this is the case the four equidistant green lines of the boric acid spectrum will be visible, and will afford conclusive evidence of the presence of boric acid.

Most borates also give the green flame coloration and the spectrum when

they are moistened with strong H_2SO_4 and held in the Bunsen-flame on a loop of platinum wire.

637. **Barium–Calcium- and Lead-salts** produce, in fairly concentrated solutions of borate, white precipitates of the metaborates, which are soluble in AmCl-solution.

638. **Hydrogen borate, or Boric acid** (H_3BO_3), usually occurs in lustrous crystalline scales. When this substance is strongly heated, it yields a fusible glass consisting of B_2O_3.

The acid is soluble both in water and in alcohol; and when these solutions are evaporated, the boric acid partially escapes with the vapour of the liquid.

The solution of boric acid turns the colour of blue litmus-paper to wine-red.

The reactions in paragraphs 634, 635 and 636 serve to detect boric acid.

CHROMATE, $(CrO_4)''$.—Use Potassium dichromate, $K_2Cr_2O_7$.

All chromates are more or less yellow or red in colour. The yellow solution of a normal chromate becomes orange-red when an acid is added, owing to the formation of a dichromate: while the reddish solution of a dichromate becomes pale yellow when it is made alkaline, owing to its conversion into normal chromate. See remarks under Chromium, paragraph 281.

639. **Reduction of Chromate to Chromic salt.**—Various substances, which readily combine with oxygen, deoxidise acidified chromate solution and produce a chromic salt; the colour of the solution at the same time changes from *orange-red* to *bright green*.

Add dilute HCl or H_2SO_4 to some chromate solution, and deoxidise a separate portion of this liquid by each of the following methods: in every case the colour of the liquid will change to bluish-green :—

(*a*) Pass H_2S into the hot solution; white S will separate owing to oxidation of the hydrogen of the H_2S.

(*b*) Add $NaHSO_3$ or H_2SO_3 and warm.

(*c*) Add alcohol and boil: the smell of aldehyde will be noticed.

(*d*) Boil for some time, after adding much strong HCl: Cl gas will be slowly evolved.

(*e*) Add Zn and warm: the reducing action of the nascent H will be slow.

The following equations show the reactions which occur with H_2S and with HCl :—

$$K_2Cr_2O_7 + 3H_2S + 8HCl = 2CrCl_3 + 2KCl + 7H_2O + 3S.$$

$$K_2Cr_2O_7 + 14HCl = 2CrCl_3 + 2KCl + 7H_2O + 3Cl_2.$$

The green solution, which results from the above reactions, will give all the reactions for a chromic salt (282–285); and since chromic acid is reduced by boiling HCl and by H_2S to chromic salt, the presence of a chromate will lead to the precipitation and detection of $Cr(OH)_3$ in the ordinary course of analysis. This chromic hydroxide, however, will be known, from the colour of the original solution, to be the result of the reduction of chromate.

640. Hydrogen peroxide, H_2O_2, or Barium peroxide, BaO_2, produces in a cold acidified solution of chromate a characteristic intense but evanescent *blue coloration* of perchromic acid.

This colour is far more permanent if ether is first added, and the liquid is then vigorously shaken immediately after the addition of the peroxide: the ether assumes and retains a blue colour.

Add a few drops of dilute H_2SO_4 to 2 c.c. of H_2O_2-solution and shake this liquid with 2 c.c. of ether: then add a little of the chromate solution and shake the liquid again. In the presence of only 0·1 milligramme of chromic acid, the upper ether layer is coloured intensely blue, and the coloration is distinctly visible when only 0·01 milligramme of chromic acid is present.

641. $Pb\bar{A}_2$: *yellow* precipitate, $PbCrO_4$: soluble in KOH, insoluble in $H\bar{A}$.

642. $AgNO_3$: *purple-red* precipitate, Ag_2CrO_4: soluble in AmOH and in HNO_3.

643. $BaCl_2$: yellowish-white precipitate, $BaCrO_4$: insoluble in $H\bar{A}$, soluble in HCl.

644. Hydrogen chromate, or Chromic acid, H_2CrO_4, has not been isolated, but is believed to be present in the reddish-yellow liquid which is produced by dissolving chromic anhydride, CrO_3, in water, or by acidifying the solution of a chromate. Its solution evolves Cl and becomes green, when it is boiled with HCl. When solution of chromic acid is neutralised by an alkali it becomes yellow, and the yellow solution yields the above reactions for chromate.

SILICATE, $(SiO_3)''$.—Use solution of Sodium silicate, or Water-glass, Na_2SiO_3; and finely-ground sand for a solid.

Silica, or silicic anhydride, SiO_2, occurs in nature as quartz, rock crystal, flint and sand.

645. HCl, if it is added drop by drop to solution of a silicate, which is meanwhile constantly stirred or shaken, will give a gelatinous precipitate of orthosilicic acid, H_4SiO_4, unless the solution is very dilute. Since the silicic acid may remain in solution, however, the non-appearance of a precipitate does not prove the absence of a silicate.

The solution of silicate, which is used for these reactions (1412), is made of such strength that acids do not cause a precipitate in it; but if some of the solution is boiled down to a quarter of its volume, the precipitate will usually be obtained on the addition of an acid.

646. Separation and Detection of SiO_2.—If silicate is present in small quantity, or is in dilute solution, it may be detected by acidifying the solution with HCl and evaporating the liquid to dryness in a porcelain dish. The evaporation is finished on the

water-bath (38), and the residue is heated on the water-bath as long as acid fumes are given off.

Insoluble SiO_2 is thus produced, and remains as a white powder when the dry residue is stirred and warmed with strong HCl.

During the last part of the evaporation over a flame, after the silica has separated as a gelatinous mass, spirting will occur unless the heat is lessened and the residue is stirred with a glass rod. This spirting may be also prevented by finishing the evaporation upon a water-bath (38) as soon as the liquid thickens.

The SiO_2, which is left undissolved by HCl, is invisible as long as the liquid remains in the porcelain dish. It is rendered visible by stirring the liquid and at once pouring it out into a glass vessel. If it is free from other substances this silica will entirely disappear when it is warmed in a platinum vessel with HF-solution and strong H_2SO_4 :—$SiO_2 + 4HF = SiF_4 + 2H_2O$.

647. **Silicates insoluble in water** may be made to yield SiO_2 as is described below (*a*, *b*), the treatment depending on their behaviour with acids.

(*a*) *Silicates decomposable by Acid.*—Many natural and artificial silicates are decomposable by evaporation with HCl, the silica being left in an insoluble condition.

The finely powdered silicate is mixed for this purpose with dilute HCl and the liquid is evaporated to dryness on the water-bath. The residue is moistened with strong HCl, then heated gently, mixed with hot water, and the liquid is boiled and filtered. White SiO_2 will be left on the filter and the filtrate will contain the metals from the silicate in solution as chlorides.

(*b*) *Silicates not decomposable by Acid.*—Many silicates belong to this class, such as mica, felspar, glass, and porcelain.

In order to remove the silica from these silicates, the finely-powdered silicate is mixed with four times its weight of fusion mixture and heated in a platinum crucible or on the foil in a powerful flame. Bubbles of carbon dioxide will be given off at first, and when these cease to escape, the temperature may be raised and the mass kept fluid for about ten minutes. It is then allowed to cool and is heated with HCl: the whole is then evaporated to dryness, the residue is moistened with strong HCl, which is then diluted with water, and the SiO_2 is separated by filtration. The metals of the silicate will now be present in the filtrate as chlorides with the alkaline chlorides.

648. **Microcosmic-bead.**—When either a silicate or SiO_2 is fused into a bead of *microcosmic salt*, $NaAmHPO_4.4H_2O$, it is not wholly dissolved, but the SiO_2 floats about in transparent particles in the melted bead, and is visible as little opaque masses when the bead is cold. The particles of SiO_2 are usually most easily seen while they are in motion in the fused bead.

649. **Na_2CO_3 in Blowpipe-flame.**—If solid SiO_2 or a silicate is heated in a fused bead of Na_2CO_3, it causes frothing: this is due to the evolution of CO_2 :—$Na_2CO_3 + SiO_2 = CO_2 + Na_2SiO_3$.

650. **Am_2CO_3, or AmCl**, produces a gelatinous precipitate of silicic acid, H_2SiO_3, which usually forms only after a time.

651. Certain silicates become blue if they are moistened with cobalt nitrate solution and are then heated on charcoal in the outer blowpipe-flame.

652. **Hydrogen silicate, or silicic acid, H_2SiO_3,** can exist in solution in water, and the solution has a faintly acid reaction. It is ordinarily met with, however, in the hydrated state as a colourless gelatinous substance, which does not affect the colour of litmus.

In this gelatinous form silicic acid is almost insoluble in water, and is only very slightly soluble in acids; but it dissolves readily as an alkaline silicate, in solution of caustic alkali or of alkaline carbonate.

When the gelatinous hydrated acid is strongly heated, it yields a white insoluble powder, SiO_2, which gives the reactions in paragraphs 648, 649, and is entirely volatilised when it is warmed in a platinum vessel with HF-solution and strong H_2SO_4.

FLUORIDE, $(F)'$.—Use finely-powdered CaF_2.

The ordinary tests for a fluoride depend upon the liberation of hydrofluoric acid, which is then allowed to act upon a glass surface and to *etch* or corrode it.

653. **Strong H_2SO_4,** if it is warmed with a little finely-powdered fluoride in a test-tube, liberates HF. This acid etches the glass, and causes the sides of the tube to throw off the liquid when it is shaken up, as a greasy surface throws off water.

If the cooled mixture is washed out of the tube and the inside of the tube is perfectly dried, the glass will be seen to be dimmed and roughened. Gentle friction with a glass rod will often detect the roughness of the etched surface, even when this is not perceptible to the eye.

654. **Etching a Watch-glass.**—The preceding test is made much more delicate if it is carried out as follows.

A watch-glass is carefully heated by holding it in crucible-tongs at some distance above a flame. Its convex surface is then rubbed with a piece of paraffin-wax, and is thus covered with a melted layer. This layer is made uniform by once more heating the glass, allowing any excess of wax to drop off, and then keeping the glass moving while it cools. The coating of wax is finally hardened by immersing the glass for a short time in cold water.

Lines or characters are now traced in the wax, near the middle of the glass, by gentle pressure with the point of a penknife; the object being simply to remove the wax from these parts, and not to scratch the glass.

When the glass has been thus prepared, it is placed, with its coated surface downwards, as a cover to a platinum crucible or small leaden cup which contains a little finely-powdered fluoride and strong sulphuric acid.

Some cold water is then poured into the glass in order to keep it cool, and the bottom of the vessel is heated by a very small flame; the covered vessel is then allowed to stand for about fifteen minutes.

The watch-glass is now removed, and is cleansed by holding it with crucible-tongs above the flame and quickly wiping off the melted wax.

On the clean bright surface thus obtained, the traced lines will usually be visible at once when the glass is held up to the light; but if mere traces of fluoride were present, the tracing may only become visible when the cold surface is breathed upon, and is then examined by reflected light.

655. **Formation of Silicon fluoride (SiF_4).**—The above methods do not serve for the detection of fluoride in the presence of silicate or of silica, since under these conditions the action of H_2SO_4 liberates SiF_4 instead of HF.

SiF_4 does not etch glass, but it gives rise to white fumes in moist air; and when it is passed into dilute AmOH, it yields a colourless flocculent precipitate of H_4SiO_4, and produces AmF in the solution.

The formation of the precipitate of silicic acid is sufficient proof of the presence of a fluoride; but after this precipitate has been filtered off, the AmF may also be detected in the filtrate. This is effected by adding $CaCl_2$-solution to the clear liquid, then filtering off the precipitate of CaF_2, and drying and examining it as is directed in paragraph 654.

The above method is employed for detecting fluoride in minerals which contain silica or silicate. The method is also sometimes utilised for the detection of fluoride in a substance, which has been previously intimately mixed with SiO_2 so as to render it suitable for the above test.

In order to try the reaction, a finely-powdered mixture of CaF_2 and SiO_2 may be heated with strong H_2SO_4. A small piece of marble should be dropped into the tube in which the SiF_4 is being produced: this evolves CO_2, which carries the silicon fluoride over into the AmOH-solution. The changes which occur are thus expressed by equations:—

$$2CaF_2 + SiO_2 + 2H_2SO_4 = SiF_4 + 2H_2O + 2CaSO_4.$$
$$SiF_4 + 4AmOH = H_4SiO_4 + 4AmF.$$

656. **$CaCl_2$**, when it is added to solution of fluoride (*Note*), gives an almost transparent gelatinous precipitate of CaF_2, which becomes more visible when the liquid is heated or when AmOH is added: this precipitate is slightly soluble in HCl, but is almost insoluble in $H\bar{A}$. [Difference from fluosilicate (470).]

Note.—Solution of NaF may be prepared for the above reaction, by heating some finely-powdered CaF_2 with melted fusion-mixture on platinum-foil for several minutes: then boiling the foil with the cool mass in water, filtering the solution, and acidifying the filtrate with $H\bar{A}$.

657. **Hydrogen fluoride, or Hydrofluoric acid, HF,** at temperatures above 20° C., is a colourless gas which fumes in the air, etches a glass surface, and dissolves freely in water. The solution of HF is acid in reaction, and differs from all other acids by decomposing and dissipating SiO_2 :—$SiO_2 + 4HF = SiF_4 + 2H_2O$. It therefore also decomposes silicates and must be stored in bottles of rubber or gutta percha instead of in glass, unless the glass surface has been carefully protected by a film of wax.

TUNGSTATE, (WO_4).—Paragraphs 127–131.

MOLYBDATE, (MoO_4).—Paragraphs 236–243.

SELENITE, (SeO_3).—Paragraphs 246–250, 253, 254.

TELLURATE, (TeO_4).—Paragraphs 260, 261.

TELLURITE, (TeO_3).—Paragraphs 257–259, 261.

TITANATE, (TiO_3).—Paragraphs 333–339.

VANADATE, (VO_4).—Paragraphs 391–397.

SECTION V

THE DETECTION AND ANALYTICAL REACTIONS OF ORGANIC SUBSTANCES.

666. **Introductory Remarks.**—Organic substances may be broadly defined as chemical compounds containing carbon.

When organic substances are being examined with a view to their identification, it is frequently necessary to ascertain their physical properties. Methods are therefore described in this section for determining the melting-point of a readily fusible solid, the boiling-point and density of a liquid, and the separation of liquids of different boiling-points by fractional distillation.

These descriptions are followed by an account of the methods employed for detecting the presence in organic substances of the elements carbon, hydrogen, nitrogen, sulphur, phosphorus, chlorine, bromine, and iodine.

The special analytical reactions for certain important organic substances are then described in detail. These substances include organic acid-radicles, hydrocarbons and their derivatives, alcohols and ethers, phenol and its derivatives, aldehydes and ketones, carbohydrates, glucosides, organic bases, and alkaloids.

DETERMINATION OF DENSITY, MELTING-POINT, AND BOILING-POINT.

667. **The Identification of a pure Organic Substance** is frequently aided by the determination of some of its constant physical properties, such as its density, and its melting-point if it is a solid or its boiling-point if it is a liquid.

These determinations may take the place of analytical tests, but they are more frequently used with the object of suggesting the analytical tests to be applied, or of confirming the results which have been yielded by the analytical reactions.

The determination of the melting-point or the boiling-point is also often of great value as a test of the purity of an organic substance. A solid substance will usually melt sharply at a particular temperature if it is pure; but if it is impure it will usually soften

before its melting-point is reached, and there may be a difference of several degrees between the softening-point and the temperature at which it becomes fluid.

Similarly if a pure liquid is distilled, the boiling-point will remain constant throughout the distillation, whereas a mixture will usually show a rise in the boiling-point as the distillation proceeds.

Accordingly these determinations will often decide whether a single substance or a mixture of substances is under examination.

The determination of the density of a solid substance involves accurate weighing on a chemical balance. Directions for the process are given in Section I. in *Clowes' and Coleman's Quantitative Analysis.*

The density of a liquid may be determined by accurate weighing, but the determination by means of a hydrometer (668) is much more rapid and convenient, and may be applied when a sufficient quantity of the liquid is available.

When a solid organic substance possesses a melting-point which can be observed on a mercurial thermometer, the process described in paragraphs 669 and 670 may be employed, and will be found to be rapid and simple in execution.

The determination of the boiling-point of a simple liquid, if the temperature falls within the range of a mercurial thermometer, is described in paragraph 671.

The constituent liquids of a mixture may often be separated from one another by fractional distillation (672), and the separated liquids may then be identified by their boiling-points or by other methods.

DETERMINATION OF THE DENSITY OF A LIQUID.

668. **The Hydrometer** serves to determine rapidly the density of a liquid, since it enables the process of weighing to be dispensed with. The apparatus consists of a glass or metal float (Fig. 58), which is weighted below to such an extent as to cause it to assume a vertical position when it is floating in the liquid. The stem is so graduated that the numbered mark, which is level with the surface of the liquid when the hydrometer is floating freely, shows the density of the liquid.

FIG. 58.

THE HYDROMETER.

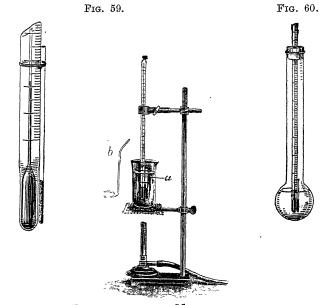
The temperature of the liquid must be adjusted to the temperature at which the hydrometer has been graduated, which is usually 15·5° C.; and all densities of liquids which are given in this book correspond to

that temperature, and are referred to the density of distilled water at 4° C. as unit, unless it is otherwise stated.

DETERMINATION OF THE MELTING-POINT OF A SOLID.

Two methods, which are commonly in use for determining the melting-point of a substance, are described below.

669. **First Method.**—The solid substance is placed in a thin-walled glass tube, which is about 1 mm. in diameter and is sealed at one end. Such a tube is readily made by drawing out a thin-walled narrow test-tube in the Bunsen-flame. The long tube thus

FIG. 59. FIG. 60.

DETERMINATION OF MELTING-POINT.

produced is cut into tubes 5 cm. in length, each of which is then closed at one end by fusion in the flame.

The open end of one of these tubes is dipped into the finely powdered substance, and the tube is placed mouth upwards and gently tapped to cause the powder to fall to the closed end. These operations are repeated until about 1 cm. of the tube is filled with the powder.

The tube is then attached closely to the stem of a delicate thermometer with the powder alongside the bulb, by binding it with fine platinum wire (Fig. 52, *a*). If the thermometer is to be dipped into water only, a little rubber ring, cut off some small rubber tubing,

may be slipped over the larger end of the tube and the thermometer stem, instead of binding it with platinum wire.

The thermometer and tube are then placed in a beaker containing a liquid which has a higher boiling-point than the melting-point of the solid. Water, strong sulphuric acid, or melted paraffin-wax may be used in the beaker, according to the temperature which is required.

The beaker is then heated until the solid melts, and the temperature of liquefaction is accurately noted by the thermometer.

During the process of heating, the contents of the beaker should be constantly mixed by means of a stirrer, which is made of bent glass rod or stout wire in the shape shown at *b* in Fig. 59. This continuous stirring is necessary, in order to secure a uniform temperature throughout the mass of the liquid during the determination.

The process should be repeated several times with fresh portions of the substance, and the mean temperature, which has been obtained from these experiments, should be taken as the melting-point of the solid. The temperature of solidification may also be noted and utilised in most cases as a check.

If the mercury-thread of the thermometer extends above the surface of the liquid, the correction which is described in the *Note* in paragraph 671 must be applied to the reading.

In the case of certain fats, and of some other substances, it is difficult to see the exact point of liquefaction. The observation is facilitated by using a tube which is open at both ends, but it is essential in this case to select a liquid for the beaker, which does not act chemically upon the substance.

If there is any difficulty in introducing the substance into this open tube, the fine end of the tube may be inserted into the melted substance, when a small quantity of the liquid will at once enter the tube by capillary attraction. This is allowed to cool and solidify, and the tube is then attached to the thermometer and immersed in the water as before.

At the moment of liquefaction, the substance will be forced up this open tube by the pressure of the liquid in the bath, and the temperature of the thermometer is noted when this movement is seen to occur.

It should be borne in mind that some substances, more especially the animal fats, show a lower melting-point when the process of fusion is repeated immediately after solidification. In such cases the normal melting-point is regained after the substance has remained in the solid condition for a sufficient interval of time.

EXPERIMENT.—The melting-point of naphthalene may be determined using a beaker which contains water for the bath. The melting-point should be approximately 80° C.

670. Second Method.—A modified form of vessel for determining melting-points is shown in Fig. 60. It is made by blowing a bulb at the end of a piece of wide glass-tube, which should be about 15 cm. in length, with a diameter of about 3 cm. and the bulb should be about 5 cm. in diameter. This bulb is nearly filled with strong sulphuric acid.

The bulb of the thermometer is then wetted with the acid by dipping it beneath the surface (Fig. 60), and the tube containing the substance is placed alongside and in close contact with the wet thermometer bulb as is shown in Fig. 59, *a* ; the tube will adhere to the wetted bulb.

The thermometer bulb with the adhering tube is then immersed in the acid, the upper part of the tube remaining above the surface of the liquid ; the small tube will continue to adhere to the thermometer owing to the surface-tension of the acid film. The stem of the thermometer is held in this position by means of a cork inserted in the mouth of the large tube, the cork having a groove cut in its edge to permit the air to escape as it is expanded by heat.

When the apparatus has been properly adjusted, heat is gradually applied to the bulb, and the melting-point is observed. The process is repeated, and the results obtained are dealt with as has been already described in the first method (669).

The discoloration of the acid, which may be caused by its continued use, may be removed by dropping in a crystal of potassium nitrate.

EXPERIMENT.—Determine the melting-point of sulphur or of benzoic acid by the above method.

DETERMINATION OF THE BOILING-POINT OF A LIQUID.

671. The Boiling-point of a simple Liquid may be determined in the following way.

The liquid is placed in a flask such as is shown in Fig. 61, the neck of which is closed by a perforated cork through which a thermometer passes, the bulb of the thermometer being close to the surface of the liquid. The liquid is then heated to boiling, and the bulb and part of the stem of the thermometer are thus surrounded by the vapour of the boiling liquid.

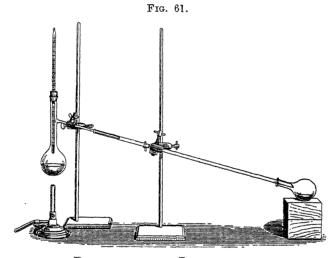
The side exit-tube in the neck of the flask should be connected with a cold-water condenser, if the liquid has a low boiling-point ; but a plain glass tube, about thirty inches in length and cooled only by the atmosphere, will suffice for less volatile liquids (Fig. 61).

As soon as the reading of the thermometer remains constant, the temperature is registered as the boiling-point of the liquid.

Note.—This reading will, however, require to be corrected if the thread of mercury in the thermometer extends above the cork. The following formula gives the correction to be added:—

$$N(T - t) \times 0{\cdot}000156.$$

Here N is the number of degrees on the thermometer-stem which are not heated by the vapour, T is the temperature indicated by the thermometer, t is the temperature taken by placing the bulb of a second thermometer midway between the top of the cork and of the mercury column during the

FIG. 61.

DETERMINATION OF BOILING-POINT.

process, this second bulb being screened from the direct heat of the Bunsen-flame, and 0·000156 is the apparent coefficient of expansion of mercury.

It should be remembered that considerable differences of atmospheric pressure will cause appreciable variations in the boiling-point. All the boiling-points which are given in this book correspond to the normal atmospheric pressure of 760 mm. of mercury.

EXPERIMENT.—The boiling-point of aniline may be taken by this method. It should be approximately 78° C., and a cold-water condenser will therefore not be required.

SEPARATION OF LIQUIDS BY FRACTIONAL DISTILLATION.

672. **Fractional Distillation** may be employed to separate from their mixture two or more miscible liquids, which differ in their boiling-points by at least 20 degrees.

If a mixture of two such liquids is placed in a distillation flask (Fig. 61), fitted with a thermometer and a cold-water condenser,

and the mixture is gradually heated, the following results will be observed.

The liquid will begin to boil at about the boiling-point of the more volatile liquid, but as the heating is continued the boiling-point will gradually rise. After a time the boiling-point will rise rapidly until it approaches the boiling-point of the less volatile liquid, when it will again rise slowly until the whole of the liquid has distilled.

If the volume of the distillate is measured from time to time, it will be found that the two largest volumes have been obtained while the thermometer indicates approximately the boiling-points of the two liquid constituents of the mixture; and that a partial separation of the constituents has therefore been effected, if the separate fractions of the distillate which come over at fairly constant temperatures have been received in separate vessels.

If each of these two main "fractions" is now separately distilled or "refractionated," it may be separated in a similar manner into fractions; and a fairly pure sample of each of the constituent liquids may be obtained by again collecting separately those fractions of the distillate which pass over while the thermometer registers the boiling-point of the particular constituent.

By a further "refractionation," or repetition of this fractional distillation, a pure specimen of each of the original liquids may ultimately be obtained.

The following example will illustrate this method of separation by fractional distillation.

EXPERIMENT.—Make a mixture of equal volumes of pure alcohol and water. Pour 150 c.c. of this mixture into the distillation-flask fitted with a thermometer and a cold-water condenser: heat the liquid gently with a naked flame, and receive the fractions which pass over between 78°–85°, 85°–92°, 92°–98°, and 98°–100° separately in four clean dry flasks.

When the volumes of these fractions A, B, C, and D, are measured, fraction A will be about one-third of the total volume, and may be proved by its smell and by its ready inflammability to contain the greater part of the alcohol.

The fractions B and C will be smaller in volume and will consist of a mixture of alcohol and water, the proportion of alcohol being so small that the mixture is not inflammable.

Fraction D will be found by its tastelessness and freedom from smell to consist almost entirely of water.

A further separation may be effected by repeating the above procedure with the fractions already obtained, until eventually the fractions with the lowest boiling-point will consist of almost

pure alcohol, and those with the highest boiling-point will consist of almost pure water.

It will be obvious that a separation of the liquids in the mixture has thus been effected, and that special methods may now be applied for the identification of each of the liquids.

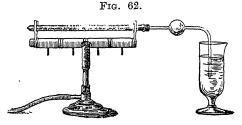
This method of procedure is often applicable to liquid mixtures, the composition of which it would be difficult or impossible to ascertain until it becomes possible to deal with each constituent of the mixture in the separate condition.

DETECTION OF THE ELEMENTARY CONSTITUENTS OF ORGANIC SUBSTANCES.

DETECTION OF CARBON.

673. **Ignition of Substance.**—The presence of carbon in an organic substance is frequently indicated, by the substance becoming charred or blackened, when it is heated alone or with strong H_2SO_4. The carbon may also be evolved as CO_2 when the substance is heated either alone or with strong H_2SO_4, and the CO_2 thus evolved may be detected by means of lime-water (474).

674. **Ignition with Copper oxide.**—A more certain and general method of detecting carbon consists in mixing the organic substance intimately with finely-powdered copper oxide (CuO), or

FIG. 62.

DETECTION OF CARBON AND HYDROGEN IN AN ORGANIC SUBSTANCE.

with some other solid oxidising compound, and heating the mixture strongly. The carbon is then wholly evolved as CO_2, and this may be detected by passing it into lime-water (474).

If perfectly dried materials are used (*Note*, 676) the process serves also for the detection of hydrogen as a constituent of the organic substance (676).

The method may be tried by mixing a little sugar with four or five times its measure of finely-powdered CuO. This mixture is then placed in the closed end of a hard glass test-tube, and the remainder of the tube is nearly filled with granular CuO. The open end of the test-tube is then fitted with a bent glass delivery-tube, and the tube is heated in a Bunsen-flame, care being taken that the granular oxide is heated to redness before the mixture is heated.

The experiment may be made in a longer tube, which is heated by the Ramsay-burner (Fig. 62), the heat being first applied to the granulated oxide, and when this is at a red heat the mixture being gradually heated to the same temperature. The delivery-tube dips into a vessel containing lime-water, which serves to indicate the evolution of CO_2.

Note 1.—In the case of a volatile liquid the apparatus must be modified so as to cause the vapour of the liquid to pass slowly over the red-hot copper oxide, the products of combustion passing on into the lime-water.

Note 2.—It must be remembered that cyanates, many carbonates, and all bicarbonates, evolve CO_2 when they are heated. Carbonates may be distinguished from other organic bodies by evolving CO_2 when they are acted upon by cold dilute acid (474).

DETECTION OF HYDROGEN.

675. **Ignition of Substance.**—Many organic substances, which contain both hydrogen and oxygen, evolve their hydrogen more or less completely in the form of steam when they are heated. If the dry substance is heated in a test-tube, and steam is evolved which condenses on the cooler part of the tube in the form of water drops, the substance is proved to contain hydrogen and oxygen.

676. **Ignition with Copper oxide.**—The presence of hydrogen in a dry organic substance may, however, be detected with greater certainty at the same time as the carbon, by the method of oxidation with dry CuO (see *Note*) at high temperature (674).

The hydrogen is completely converted by this oxidation process into steam, which condenses in the form of water drops in the cooler part of the test-tube, or in the delivery-tube. The bulb in the delivery-tube (Fig. 62, p. 181) is of advantage, since it reduces the velocity of the current of escaping gas and vapour and also exposes it more fully to the cooling action of the air, and therefore promotes the condensation of the steam.

The presence of hydrogen in sugar will have been already proved, if perfectly dry materials were used, by the production of the water,

which has condensed in the apparatus during the test for carbon (674). The test is rendered more delicate by placing some white anhydrous $CuSO_4$ in the bulb, since the white powder becomes blue in the presence of even a small amount of water.

Note.—Any moisture which is present in the substance or in the copper oxide will be evolved as steam, and will be condensed as is described above. Both the organic substance and the CuO must therefore have been perfectly dried, in order to prevent a wrong inference from being drawn as to the presence of hydrogen in organic combination in the substance.

A solid organic substance may usually be freed from moisture by heating it in the steam-oven (48) for about an hour, and the copper oxide should be dried by igniting it to redness for an hour and cooling it in a desiccator.

DETECTION OF NITROGEN.

677. **Ignition of Substance.**—Nitrogen is evolved from many organic substances in the form of ammonia, or of an alkaline organic derivative of ammonia, when the substance is heated. The ammonia, or other alkaline substance, may usually be readily detected by its pungent smell or by its alkaline action upon moist turmeric-paper (*Note*, 678).

678. **Ignition with Soda-lime.**—A general method of detecting the presence of nitrogen consists in mixing the organic substance intimately with powdered soda-lime, and then heating the mixture strongly in a hard glass test-tube. Either ammonia or a basic substance containing nitrogen, such as an amine, will be evolved, and may be detected by turning moist turmeric-paper brown.

In trying the reaction urea or albumen may be employed.

This test is applicable to most organic substances which contain nitrogen, with the exception of nitro-, nitroso-, azo-, and diazo-bodies.

Note.—It must be remembered that many ammonium compounds evolve NH_3 when they are heated, and that they all evolve NH_3 when they are heated with soda-lime. When ammonium compounds, however, are mixed with solution of KOH, they evolve NH_3 at ordinary temperatures or when they are gently heated; and they may be distinguished in this way from most organic compounds containing nitrogen, since these require to be heated much more strongly with solution of KOH, and in some cases with *solid* KOH or with soda-lime, before they evolve NH_3.

679. **Ignition with Sodium and Production of Prussian Blue.**—Another general method for the detection of organic nitrogen consists in converting the nitrogen of the substance into a soluble cyanide, and the cyanide into "Prussian blue."

The procedure is described in the following paragraph, and either urea or albumen may be used as the nitrogenous organic substance.

Heat the nitrogenous substance strongly with a small piece of

sodium or potassium in a little hard-glass ignition-tube (see *Note*) When the substance has been charred, break up the tube in some water in a mortar with the pestle, transfer the liquid with the substance to a boiling-tube, warm gently and filter. Then add a few drops of solutions of $FeCl_3$ and $FeSO_4$: and unless the liquid is already strongly alkaline to test-paper, add KOH in excess. Then boil the liquid, and add HCl in excess.

The formation of a dark blue precipitate, or of a blue or dark green solution, indicates the formation of Prussian blue; and the nitrogen, which is a necessary constituent of this Prussian blue, must have been derived from the organic substance.

This reaction is more delicate than the preceding one (678), and it serves for the detection of nitrogen in all organic substances with the exception of the diazo-compounds.

Note.—If sulphur is present, the organic substance must be mixed with iron filings, or better with "reduced iron," before it is heated with sodium.

The absence of cyanogen-compounds in the organic substance must be ascertained (692 and 694) before applying this test for nitrogen.

DETECTION OF SULPHUR.

680. The Presence of Sulphur in an organic substance may be detected by converting the sulphur either into Na_2S (681), or into Na_2SO_4 (682).

Albumen may be used in trying the following tests.

681. Ignition with Sodium, and formation of Sulphide.—Ignite the organic substance with a small piece of sodium: then extract the residue with warm water, filter the solution, and add to the filtrate, made alkaline if necessary with NaOH, some solution of sodium nitroprusside: the presence of sulphur will be indicated by *a violet coloration* (483).

Lead acetate-solution may be added instead of nitroprusside, and will produce black PbS (482); but this is a less delicate test than the nitroprusside reaction.

682. Ignition with $NaNO_3$, and formation of Sulphate.—Mix the solid organic substance in a porcelain crucible with four times its measure of dry Na_2CO_3 and its own measure of $NaNO_3$, and heat the mixture until the alkali salts are fused. Dissolve the cool product in dilute HCl, and add $BaCl_2$: *a white precipitate* of $BaSO_4$ (464) shows the presence of sulphate, which has been formed from sulphur in the organic substance.

DETECTION OF PHOSPHORUS.

683. **The Presence of Phosphorus** in an organic substance may be detected by converting the phosphorus either into PH_3 (684), or into phosphate (685).

684. **Heating with Magnesium.**—Char the substance by heat, then mix it with magnesium-powder and heat the mixture strongly. Now moisten the cold residue with water: a garlic-like smell of PH_3 will be observed, showing that magnesium phosphide has been produced during the ignition, and has then been decomposed by the water. This proves the presence of phosphorus in the original substance.

685. **Ignition with $NaNO_3$, and formation of Phosphate.**—Heat the solid substance with fused Na_2CO_3 and $NaNO_3$, as has been described for the detection of sulphur (682). Then dissolve the residue in dilute HNO_3, and add a few drops of this liquid to some $AmHMoO_4$-solution and warm gently: the formation of a yellow precipitate (571) proves that phosphate has been formed, and that phosphorus was present in the original substance.

DETECTION OF CHLORINE, BROMINE, AND IODINE.

686. **The Presence of the Halogen Elements** in an organic substance may be detected either by the flame-coloration of their copper salts (687), or by converting the halogens into sodium salts and then applying the ordinary tests to the solution of these salts (688).

Chloral may be used for trying these methods of detection of organic chlorine.

687. **Copper Flame-coloration.**—Fix a piece of CuO in a loop of platinum wire (*Note*, below), and heat it strongly in the outer Bunsen-flame until it gives no colour to the flame. Then dip the CuO into the organic substance and ignite it again, first in the inner and then in the outer Bunsen-flame: a green flame-coloration with a blue centre will appear, and will indicate the presence of chlorine in the organic substance.

A similar result is obtained if the organic substance contains either bromine or iodine. This test, therefore, only serves to indicate the presence of a halogen, and does not distinguish between the different halogen elements.

Note.—The expensive platinum wire may be replaced by a piece of fine copper wire: this must be superficially oxidised by heating it in the outer flame, and is then dipped into the organic substance.

688. Ignition with Soda-lime or with Sodium.—Mix a little of the organic substance with soda-lime free from chloride, place the mixture in a hard glass test-tube, and add a layer of soda-lime. Then heat the soda-lime to redness (Fig. 62 p. 181), and gradually extend the heating to the mixture until the whole is red hot. Now allow the whole to cool, and dissolve the cold soda-lime in dilute nitric acid. Test this clear solution for chloride, bromide and iodide in the ordinary way (539–556).

The substance may be ignited with a small piece of sodium, instead of with soda-lime, and the clear solution obtained by extracting the cold residue with water is then examined for the halogens in the ordinary way, 539–556. It must be remembered that the process of ignition with sodium will produce a cyanide if nitrogen was present in the substance, and that this might be mistaken for a halide (679, 691, *et seq.*).

ANALYTICAL REACTIONS OF ORGANIC SUBSTANCES.

GROUP I.—ORGANIC ACID-RADICLES.

1. CYANOGEN ACID-RADICLES.

This Group of acid-radicles includes cyanides, cyanates, thiocyanates, ferrocyanides and ferricyanides.

CYANIDE, (CN′, or Cy′).—Use freshly-made solution of KCN.

The alkaline cyanides smell faintly of bitter almonds, the smell being due to the liberation of HCN by the action of the CO_2 and H_2O in the air. Hydrocyanic acid is intensely poisonous.

689. **Dilute acids** liberate HCN with an odour of bitter almonds; great care should be taken not to inhale this acid vapour to any extent, it should be only cautiously wafted to the nose with the hand. Certain complex cyanides, such as K_4FeCy_6 and K_3FeCy_6, also evolve HCN when they are treated with dilute acid (705, 712).

690. **Strong H_2SO_4**, when it is warmed with any cyanide, whether it is simple or complex, causes decomposition with evolution of CO, which burns with a blue flame.

691. **$AgNO_3$**: a white precipitate of AgCN.

This precipitate is most easily obtained by pouring a drop of the KCN-solution into the $AgNO_3$-solution.

Show with three separate portions of the precipitate in the liquid, that the precipitate is soluble in KCN-solution when it is added in excess, and in AmOH, but is insoluble in dilute HNO_3.

Filter off some of this precipitate, and wash it with hot water, until it is proved to be free from $AgNO_3$ by HCl causing no milkiness with the last few drops of the washing water. Then dry it, scrape it from the filter into a porcelain crucible, and heat it strongly; metallic silver will remain. If the cool residue is warmed with a little dilute HNO_3 it will dissolve, giving off reddish brown gas; and when a drop of HCl is added to this solution, a curdy precipitate of AgCl will be produced.

This method of examining the precipitate which has been produced by $AgNO_3$ distinguishes AgCN from AgCl, AgBr, and AgI; these are also precipitated by $AgNO_3$ and are insoluble in HNO_3, but when they are dried and strongly heated, they fuse without undergoing decomposition. Hence, when HNO_3 is warmed with the cool mass after fusion, it cannot dissolve out Ag;

and when HCl is added to the HNO_3, it either gives no precipitate, or it causes only a slight milkiness, which is due to the precipitate not having been perfectly freed from soluble silver salt.

This process of proving the silver precipitate to consist of AgCN is somewhat tedious and need seldom be used, since cyanide is readily detected and distinguished by the following reactions.

692. **"Prussian Blue" test.**—$FeSO_4$-solution and $FeCl_3$-solution are added to solution of cyanide, and the liquid is then made distinctly alkaline with KOH, and boiled; it is then cooled and acidified with HCl: "*Prussian blue*," $Fe_4(FeCy_6)_3$, will be formed, and will appear as a deep blue precipitate: or if the quantity of cyanide originally present was small, a bluish-green solution of the Prussian blue will be obtained.

If no cyanide is present, the addition of HCl will produce an almost colourless and perfectly clear liquid.

693. **Formation of Thiocyanate, or Sulphocyanide, AmCNS.**—If dilute H_2SO_4 is added to a cyanide in a test-tube fitted as is shown in Fig. 56, 474, and then a small piece of marble is dropped in and the liquid is boiled, HCN will be carried over by the CO_2 gas; and if the gas is allowed to bubble through some Am_2S-solution, AmCNS will be formed.

If the Am_2S-solution is now boiled in a porcelain dish, and acidified when cold with HCl in order to remove unchanged Am_2S, the addition of several drops of $FeCl_3$ will produce a red colour (703). The colour will be easily seen against the interior of the white dish. This result proves that HCN has passed into the Am_2S, and therefore that cyanide was present in the original substance.

A little of this red liquid should be added to some $HgCl_2$-solution. If the red colour is destroyed, the presence of a thiocyanate is confirmed.

When HCl is added to the Am_2S in the above reaction, white S will separate. If the yellow liquid has been previously boiled in a porcelain dish until it becomes colourless, filling in distilled water to prevent evaporation to dryness, the separation of S on the addition of an acid is prevented. But this separation of S is frequently advantageous, since its whiteness helps to show up even a faint reddish tint in the liquid.

The marble is added in order to cause evolution of CO_2 gas: the escape of the gas lessens the risk of the Am_2S being sucked back during the reaction: it also helps to carry over the HCN into the Am_2S-solution, and to prevent it from remaining behind in the test-tube.

694. **The formation of Thiocyanate** can often be more simply secured, by boiling the solution of the cyanide in a porcelain dish with yellow Am_2S. The Am_2S must be added until the yellow colour of the mixture remains after the liquid has been boiled for a short time. If a dark-coloured precipitate is formed, the yellow colour of the liquid can only be seen after the precipitate has been

removed from a portion of the liquid by settling or by filtration.

The whole of the liquid is then filtered, if necessary, and is acidified with HCl in the porcelain dish, and $FeCl_3$ is added in small quantity: a blood-red colour will be produced, which will not be removed when the liquid is heated or is mixed with a little dilute HCl. The colour will be at once destroyed, however, when a few drops of the liquid are added to some $HgCl_2$-solution.

Note.—The methods described in paragraphs 692, 693, 694 serve as exceedingly delicate tests for cyanide. The methods in 692 and 693 are often less readily performed than that in 694, but they exceed it in delicacy. The method in 694 is only replaced by that in 693 in cases where the filtrate is dark coloured after the substance has been boiled with an excess of Am_2S, and the red coloration would therefore be invisible.

The results of the reactions in paragraphs 692, 693 and 694 are also given by many complex cyanides.

695. **$HgCy_2$ and AgCy do not show the Reactions for Cyanide** by methods 691, 692, 693, but when they are boiled with Am_2S, according to method 694, AmCNS will remain in the filtrate from the black precipitate of sulphide, and will give the red coloration with $FeCl_3$.

When solid $HgCy_2$ is heated in a small tube closed at one end, it gives off cyanogen gas, which burns with a peach-blossom coloured flame if it is kindled. This gas is *very poisonous* when it is inhaled.

696. **Hydrogen cyanide, Hydrocyanic acid or Prussic acid, HCN,** is a colourless, volatile, inflammable liquid which boils at 26° C. It readily dissolves in water, and the vapour emitted from the acid or its solution smells like bitter almonds. The acid is *highly poisonous* when it is inhaled as vapour or swallowed as liquid. Hydrocyanic acid is detected by (691–694).

CYANATE, (CNO)′.—Use a freshly-made cold solution of KCNO.

697. The cyanates of the alkalis and alkaline earths are stable in the dry state, but they change in moist air or in solution to a mixture of bicarbonate and ammonia.

698. **Dilute Sulphuric acid** sets free cyanic acid, which gives an irritating and pungent odour. The acid decomposes into an ammonium salt and carbon dioxide:—$HCNO + H_2O = CO_2 + NH_3$; hence CO_2 mixed with a small amount of pungent HCNO is given off with effervescence, and the solution contains Am_2SO_4, which will evolve ammonia when it is warmed with KOH.

699. **$AgNO_3$:** white curdy precipitate, AgCNO, soluble in AmOH and in HNO_3. (Difference from cyanide.)

700. **Cobalt acetate** is coloured blue by a solution of the cyanate, owing to the formation of blue potassium cobaltocyanate, $K_2Co(CNO)_4$.

THIOCYANATE, OR SULPHOCYANIDE, (CNS)′.—Use solution of KCNS.

701. **Moderately strong H_2SO_4** decomposes thiocyanates with

evolution of COS, which burns with a blue flame :—$KCNS + H_2SO_4 + H_2O = COS + KHSO_4 + NH_4HSO_4$.

702. **$AgNO_3$:** white curdy precipitate, AgCNS, soluble in AmOH, insoluble in HNO_3.

703. **$FeCl_3$:** blood-red coloration, but no precipitate: the colour is weakened but not destroyed by HCl : it disappears entirely when the liquid is dropped into $HgCl_2$-solution. [Difference from similar colorations produced by other acid-radicles.]

704. **$CuSO_4$,** added drop by drop, gives first an emerald green liquid and then a black precipitate of $Cu(CNS)_2$.

If sulphurous acid is then added, white CuCNS is produced from the black $Cu(CNS)_2$. If H_2SO_3 is added before the $CuSO_4$ to the sulphocyanide solution, the white precipitate is at once produced.

FERROCYANIDE, $(FeCy_6)^{IV}$.—Use solution of $K_4FeCy_6.3H_2O$.

705. **Dilute H_2SO_4** produces no change at ordinary temperatures ; but when it is heated to boiling, HCN is evolved :—

$$2K_4FeCy_6 + 3H_2SO_4 = K_2Fe.FeCy_6 + 3K_2SO_4 + 6HCN.$$

706. **Strong H_2SO_4** decomposes ferrocyanides completely with evolution of CO :—

$$K_4FeCy_6 + 6H_2SO_4 + 6H_2O = 6CO + 2K_2SO_4 + FeSO_4 + 3Am_2SO_4.$$

707. **Strong HCl :** white precipitate of H_4FeCy_6, which gradually changes to blue.

708. **$FeCl_3$:** dark blue precipitate of "*Prussian blue,*" $Fe_4(FeCy_6)_3$, insoluble in HCl, soluble in $H_2C_2O_4$ to a dark blue liquid, and changed by KOH into brown $Fe(OH)_3$.

The solubility in $H_2C_2O_4$, and the insolubility in HCl, may be shown by pouring off portions of the liquid containing the precipitate, heating them with HCl and with $H_2C_2O_4$ respectively, then filtering and noting that the filtrate is rendered blue by the solution of the precipitate.

709. **$FeSO_4$:** light blue precipitate, $K_2Fe(FeCy_6)$; which becomes darker in colour by oxidation on exposure to the air, or on the addition of Cl- or Br-water, or when it is warmed with HNO_3, owing to the formation of Prussian blue (708).

710. **$CuSO_4$:** a chocolate-coloured precipitate, Cu_2FeCy_6, insoluble in HĀ. This is very characteristic.

711. **$AgNO_3$:** white precipitate, Ag_4FeCy_6, insoluble in HNO_3

and in AmOH. When the precipitate is heated with HNO_3, it changes to orange-red Ag_3FeCy_6 which is *soluble in AmOH.*

FERRICYANIDE, $(FeCy_6)'''$.—Use fresh K_3FeCy_6 solution.

A ferricyanide may be prepared by oxidising a ferrocyanide by means of Cl, Br, H_2O_2 or other suitable oxidant.

712. **Dilute and strong H_2SO_4** behave with ferricyanides in the same manner as with ferrocyanides (705, 706).

713. **$FeCl_3$:** dark green or brown coloration; no precipitate is formed, the liquid becoming transparent on dilution.

714. **$FeSO_4$:** dark blue precipitate of "*Turnbull's Blue,*" $Fe''_3(FeCy_6)_2$, insoluble in acids: KOH destroys the blue colour.

715. **$CuSO_4$:** yellowish precipitate.

716. **$AgNO_3$:** orange-coloured precipitate, Ag_3FeCy_6, insoluble in HNO_3, *soluble in AmOH*: a white residue undissolved by AmOH proves that some K_4FeCy_6 was originally present (711).

717. **Detection of Ferro- and Ferricyanide.**—Ferro- and ferricyanide can be found and distinguished by pars. 708–710 and 713–715, or by the precipitate given by $AgNO_3$ in the solution acidified with HNO_3. This precipitate will have a more or less decided orange-red colour if a ferricyanide is present.

If the precipitate is separated from most of the liquid by filtration or decantation and is gently heated with AmOH, white Ag_4FeCy_6 will be left if a ferrocyanide was present, and when the filtered ammoniacal liquid is acidified with HNO_3 orange-red Ag_3FeCy_6 will be reprecipitated.

Another method for detecting cyanide, ferrocyanide, ferricyanide and thiocyanate in the presence of one another is given in paragraph 1284.

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725. **Introductory Remarks on other Acid-radicles.**—The other acid-radicles whose reactions are described in this Section are all radicles of carboxylic acids, with the exception of urates (807).

Pyrogallic acid, picric acid, and carbolic acid are more correctly termed pyrogallol, trinitrophenol and phenol respectively: and their reactions are described under phenol derivatives (848–871), as they are not true acids.

Carboxylic acids are characterised by containing the monovalent carboxyl group COOH, in which the hydrogen atom is replaceable by a metal. These acids are usually weak acids, and are only slightly dissociated by solution.

In aqueous solution the organic acid R·COOH is dissociated into

the ions H˙ and R˙COO′ : thus acetic acid, $CH_3.COOH$, is separated into the ions H˙ and CH_3COO', and succinic acid, $C_2H_4(COOH)_2$, into the ions 2H˙ and $C_2H_4(COO)_2''$. It is evident therefore that the basicity of the acid corresponds to the number of COOH-groups which are present in its molecule.

The organic acids themselves are often available for trying the reactions : the corresponding salts of the alkali-metals are usually obtainable, and less frequently the salts of organic bases or of heavy metals. The tests may be applied directly to the salts of the alkali-metals : but the free acids must be neutralised with sodium hydroxide, since a neutral solution is used when possible for trying the reactions.

In the following statement the general character and properties of each acid are first described, and then the most important reactions of its salts are given.

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2. ALIPHATIC ACID-RADICLES.

The acid-radicles of this class, whose reactions are described are formate, acetate, oxalate, succinate, malate, tartrate and citrate,

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FORMATE, $(CHO_2)'$.—Use Sodium formate, $NaCHO_2$.

Formic acid and formates much resemble acetic acid and acetates.

726. Formic acid, H.COOH, is a colourless fuming liquid, with a pungent smell ; it boils at 100·6° C., has a density of 1·2256, and is readily miscible with water, with alcohol, and with ether. The acid and its salts are powerful reducing reagents.

All the formates, with the exception of the formates of Pb and Hg, are readily soluble in water.

727. Ignition.—A solid alkaline formate fuses and chars and emits CO and CO_2, when it is strongly heated. If it is heated with soda-lime hydrogen is evolved.

728. H_2SO_4 : when a formate is heated with strong H_2SO_4, it evolves CO gas, which burns with a blue flame. No charring or blackening occurs, and no CO_2 is evolved, as in the case of an oxalate (739).

If a formate is distilled with *dilute* H_2SO_4, a distillate is obtained which emits the pungent smell of formic acid.

729. $FeCl_3$ imparts a deep red colour to the solution of a formate ; the coloration is destroyed by the addition of HCl.

When the red liquid containing excess of formate is boiled, the Fe is completely precipitated as basic ferric formate, and the liquid becomes colourless. This reaction is precisely similar to that for acetate (736).

730. **Silver mirror.**—When solution of a formate is gently heated with ammoniacal solution of $AgNO_3$ (*Note*, 759), it gives no silver mirror. But free formic acid, or solution of a formate which has been acidified with $H\bar{A}$, gives a silver mirror when it is heated with $AgNO_3$-solution.

731. **$HgCl_2$**, when it is mixed with solution of a formate and heated to about 70° C., yields a white precipitate of Hg_2Cl_2, if HCl and alkaline chlorides are absent.

ACETATE, $(C_2H_3O_2)'$ or $(\bar{A})'$.—Use Sodium acetate, $Na\bar{A}.3H_2O$.

732. **Acetic acid, $CH_3.COOH$,** is known as *glacial acetic acid.* At temperatures below 16·7° C. it is a colourless crystalline substance, which melts at 16·7°, and boils unchanged at 118° C., giving off a very pungent inflammable vapour. This acid does not redden blue litmus test-paper until it is diluted. It is miscible with water, with alcohol, and with ether in all proportions.

The acetates, with the exception of acetates of $Hg^{\cdot}$ and Ag and a few basic acetates, are soluble in water.

733. **Ignition.**—Many solid acetates, when they are strongly heated, blacken and evolve the vapour of acetone; this vapour possesses a peculiar smell, and burns with a bright flame when it is kindled.

734. **Strong H_2SO_4,** when it is heated with an acetate, evolves vapour of $H\bar{A}$. This vapour, if it is smelt in an undiluted state, is very pungent; in mixture with air it smells like vinegar.

735. **Formation of Ethyl acetate.**—If an acetate is first mixed with a little alcohol, and then with strong H_2SO_4, a fragrant smell of ethyl acetate, $C_2H_5\bar{A}$, will be emitted when the mixture is warmed. The smell is most pronounced when the liquid is allowed to cool for a short time, and is then shaken up.

736. **$FeCl_3$,** if it is added in small quantity to solution of an acetate, causes *a deep red coloration.*

The red colour of the solution is changed to yellow by the addition of a few drops of dilute HCl; it is distinguished in this way from the coloration which has been caused by thiocyanate (703).

If the red liquid contains an excess of the acetate and is boiled, the Fe is completely precipitated as light brown basic acetate, and the liquid becomes colourless.

737. **Cacodyl reaction.**—This reaction must be carried out with due caution, since the vapour of cacodyl is very poisonous.

When a solid acetate is heated with a minute quantity of As_4O_6 the disgusting smell of the vapour of cacodyl, $As(CH_3)_2$, is evolved.

OXALATE, $(C_2O_4)''$.—Use Ammonium oxalate, $Am_2C_2O_4.2H_2O$.

738. **Oxalic acid, $(COOH)_2.2H_2O$,** crystallises in colourless rhombic crystals, which are soluble in water and in alcohol, and slightly soluble in ether: the aqueous solution is poisonous. The acid melts at 98° C., and at 150° C. it partly sublimes unaltered evolving vapour which causes coughing, and is partly decomposed:—$H_2C_2O_4 = H.COOH + CO_2$. It yields the reactions in paragraphs 739–743.

Most oxalates are insoluble in water.

739. **Strong H_2SO_4,** if it is heated with a solid oxalate, causes an effervescence, which is due to the evolution of a mixture of CO and CO_2:—

$$Am_2C_2O_4 + 3H_2SO_4 = CO + CO_2 + 2AmHSO_4 + H_2SO_4.H_2O.$$

The CO may be detected by burning with a blue flame when a light is applied, and the CO_2 is found by rendering lime-water milky (474, 1, 3, 4).

No blackening or charring is caused by strong H_2SO_4. Oxalates differ in this respect from most other organic acids and their salts.

740. **Solution of $CaCl_2$, of $CaSO_4$, or of CaH_2O_2,** when it is added to solution of an oxalate, gives a white precipitate of CaC_2O_4, which is insoluble in AmOH and in $H\bar{A}$, but soluble in HCl and in HNO_3. Keep this precipitate.

741. **Conversion into Carbonate by Ignition.**—Filter off the above precipitate of CaC_2O_4 (740), and pour upon part of it some dilute HCl; it will not effervesce.

Dry the remainder of the precipitate, and heat it for a moment to dull redness on platinum foil; it will be converted *without blackening* into $CaCO_3$, and this will effervesce when dilute HCl is poured upon it.

This is a general test for oxalate of K, Na, Ba, Sr, or Ca; since each of these oxalates, when it is ignited, leaves a carbonate which effervesces with an acid. Many other organic salts of these metals undergo a precisely similar change when they are ignited, but the change of these other salts is usually attended by charring.

742. **Evolution of CO_2 by Oxidation.**—When an oxalate, either in the solid state or in strong solution, is heated with MnO_2 (*Note*) and H_2SO_4, it evolves CO_2:—

$$Am_2C_2O_4 + MnO_2 + 3H_2SO_4 = 2CO_2 + MnSO_4 + 2AmHSO_4 + 2H_2O.$$

Note.—If the MnO_2, which is to be used in the test, is not known to be free from carbonate, it is best to add a little H_2SO_4 to the MnO_2 in a test-tube and then heat the liquid. If CO_2 is found in the tube (474, 1, 3, 4) the heating should be continued, and the CO_2 should be removed occasionally by sucking fresh air into the test-tube through a glass tube which is pushed down near to the surface of the liquid.

As soon as no CO_2 can be detected in the tube after it has been heated for a short time, the liquid being still distinctly acid, the oxalate is added and the mixture is again heated. CO_2 will be rapidly given off from the oxalate, and may be detected by the ordinary methods.

743. **$KMnO_4$**-solution, acidified with dilute H_2SO_4, is decolorised in the cold by a soluble oxalate. (Difference from other organic acids.)

744. **$AgNO_3$** gives a white precipitate of $Ag_2C_2O_4$, which does not darken in colour when the liquid is heated.

SUCCINATE, $(C_4H_4O_4)''$.—Use Ammonium succinate, $Am_2C_4H_4O_4$.

Succinate and benzoate closely resemble one another in their analytical reactions; the differences are therefore important.

745. **Succinic acid,** $C_2H_4(COOH)_2$, crystallises in monoclinic prisms, which melt at 184° C.: it is readily soluble in water, in alcohol and in ether; but it is insoluble in chloroform. (Difference from benzoic acid.)

746. **Ignition.**—When succinic acid is heated in an ignition-tube it emits fumes of succinic anhydride, which are very irritating to the throat and cause coughing when they are inhaled.

The anhydride condenses as a white sublimate on the cold upper part of the tube.

747. **$KHSO_4$,** when it is heated with a solid succinate in an ignition-tube, yields a sublimate of succinic acid in oily drops, which crystallise on cooling.

748. **$BaCl_2$ solution,** when it is added together with AmOH and much alcohol, precipitates white $BaC_4H_4O_4$. (Difference from benzoate.)

A similar difference is shown with $CaCl_2$

749. **$FeCl_3$** gives a *reddish-brown* precipitate of basic ferric succinate, which is soluble in mineral acid, but is insoluble in $H\bar{A}$.

MALATE, $(C_4H_4O_5)''$.—Use solution of Malic acid, $H_2C_4H_4O_5$, which has been carefully neutralised by NaOH.

750. **Malic acid,** $CH_2 \cdot CHOH(COOH)_2$, is a colourless, crystalline, deliquescent substance, having a pleasant sour taste: it is readily soluble in water and in alcohol, but not in ether.

When the acid is heated in an ignition-tube it melts at 100° C., and at 180° C. it yields at first malic and fumaric acids; and when it is heated to higher temperatures it chars and evolves CO and CO_2. The crystals have a density of 1·56.

751. **Strong H_2SO_4,** when it is heated with a malate, evolves CO and CO_2, and the liquid gradually darkens.

752. **$CaCl_2$:** the addition of $CaCl_2$, followed by boiling or by the addition of alcohol, produces a white precipitate in a neutral solution. This precipitate is soluble in AmOH. (Difference from citrate.)

753. **$Pb\bar{A}_2$** gives a white precipitate, which fuses and then dissolves when it is heated with sufficient water. If this precipitate is transferred to a piece of porcelain and heated, it swells up into a light puffy mass.

754. **$AgNO_3$** gives a white precipitate, which becomes grey when it is heated.

TARTRATE, $(C_4H_4O_6)''$ or ($\bar{\bar{T}}$).—For a neutral tartrate, use $KNa\bar{\bar{T}}$; for an acid tartrate, $H_2\bar{\bar{T}}$ or $NaH\bar{\bar{T}}$.

755. **Tartaric acid,** $(CHOH)_2(COOH)_2$, forms colourless rhombic crystals, which are not altered by exposure to the air. It melts at 170° C., has a pleasantly sour taste, and is soluble in water and in alcohol, but not in ether. The acid is detected by being heated either alone or with strong H_2SO_4 (756, 757, 764); and its solution, if neutralized, yields the reactions in paragraphs 758–763.

The normal salts of the alkali-metals are soluble in water, but the acid salts of K and Am are almost insoluble.

756. **Ignition.**—When a solid tartrate is heated strongly in a tube, it chars and gives off a smell of burnt sugar, leaving a residue of the carbonate or the oxide of the metal mixed with carbon.

757. **Strong H_2SO_4,** when it is heated with a solid tartrate, causes rapid blackening and evolution of a mixture of CO, CO_2 and SO_2.

Accordingly if the mixed gases are passed successively through $K_2Cr_2O_7$-solution and through lime-water, SO_2 and CO_2 will be detected (474, 489), and the residual stream of CO gas may be kindled and will burn with the characteristic blue flame of CO.

758. **$AgNO_3$** produces in the strong solution of a neutral tar-

trate a white curdy precipitate of $Ag_2\bar{T}$, which is soluble in AmOH and in HNO_3. Keep this precipitate.

759. **Production of a Silver mirror.**—Allow some of the precipitate from the preceding reaction to settle in a test-tube, and decant as much of the clear liquid as possible.

Then pour *very dilute* AmOH drop by drop into the tube, until the precipitate, after it has been shaken up with the liquid, is nearly but not quite dissolved.

Now place the test-tube in some cold water in a beaker, and heat the water to about 60°. A brilliant mirror-like film of Ag will be deposited upon the interior of the tube.

Note.—If the original solution of the tartrate is dilute, the mirror is most easily obtained as follows. Very dilute AmOH is added to solution of $AgNO_3$ until the precipitate which forms at first is nearly redissolved; this reagent is added to the neutral tartrate solution, and when the mixture is warmed, the mirror will be formed.

If the liquid is quickly boiled, instead of being gradually heated short of boiling, the Ag will be deposited as a dull black precipitate, which does not adhere to the glass and is not characteristic.

760. **$CaCl_2$** precipitates from the solution of a neutral tartrate white or crystalline $Ca\bar{T}$: this precipitate often separates only after the liquid has been shaken well, and has then been allowed to stand for a time. It is soluble in acids, and its formation is retarded by the presence of AmCl or of an Am-salt.

When this precipitate is freshly formed, it is completely soluble in strong cold KOH-solution which is free from K_2CO_3. If this alkaline solution of the tartrate is boiled, the $Ca\bar{T}$ is reprecipitated; but it dissolves again, more or less completely, when the liquid is cold.

Decant the clear liquid from the $Ca\bar{T}$-precipitate, and pour upon the precipitate a little very dilute AmOH. Then drop in a small crystal of $AgNO_3$ and heat slowly. A silver mirror will form on the part of the glass on which the crystal of $AgNO_3$ rests.

761. **KCl, or better $K\bar{A}$,** if it is added to the solution of an acid tartrate, or to solution of a neutral tartrate which has been acidified with $H\bar{A}$, gives a white crystalline precipitate of $KH\bar{T}$; this precipitate forms slowly unless the liquid is vigorously stirred or shaken.

The precipitate is soluble in caustic alkalis and in mineral acids, but is almost insoluble in alcohol; hence alcohol is often added to hasten the precipitation.

762. **$FeCl_3$ solution,** if it is added in small quantity to solution of a tartrate, undergoes no precipitation when the liquid is made strongly alkaline by the addition of KOH or AmOH.

The precipitation of several other metals, such as Al, Mn and Cu, from their solutions by alkaline hydroxides, is similarly prevented by the presence

of a tartrate. This is owing to the formation of a double tartrate, which is not decomposed by the alkali.

763. **Hydrogen peroxide.**—If a few drops of the peroxide are added to a tartrate solution, then some $FeSO_4$-solution and excess of KOH, a *violet coloration* will be produced. (Difference from citrate.)

NaOCl-solution, instead of H_2O_2, may be added to the tartrate solution which has been previously acidified with $H\bar{A}$.

764. **Resorcinol.**—If a minute quantity of a solid tartrate is mixed with twice its volume of resorcinol and about 2 c.c. of strong H_2SO_4 and the mixture gently heated, a bright red coloration is produced. If pyrogallol is substituted for the resorcinol a purple coloration is produced. (Distinction from citrate.) Tartar emetic answers to this test, but not to some of those which are given above.

CITRATE, $(C_6H_5O_7)'''$.—Use Sodium citrate, $Na_3C_6H_5O_7.2H_2O$.

765. **Citric acid, $C_3H_4(OH)(COOH)_3.H_2O$,** crystallises in transparent rhombic prisms. It is very soluble in water, less soluble in alcohol, and only slightly soluble in ether. When the acid is heated to 100° C. it loses its water of crystallisation and becomes anhydrous: it then fuses at 153° C., forms aconitic acid at 175° C., and finally blackens, giving off irritating fumes.

766. A citrate resembles a tartrate and an oxalate in its reactions; it differs by emitting pungent acid fumes when it is carbonised by heat, and by darkening when it is heated with strong H_2SO_4, but only after the mixture has been heated for some time and inflammable gases have escaped.

Citrate differs from tartrate by giving no precipitate with $K\bar{A}$-solution (761), and by yielding no distinctive colours in the reactions in paragraphs 763, 764.

767. **$CaCl_2$, or Lime-water.**—Calcium citrate is precipitated by the addition of either a large excess of lime-water, or of a mixture of AmOH, AmCl and $CaCl_2$, but only *after long standing or when the liquid is boiled.* This precipitate is insoluble in KOH. (Difference from $Ca\bar{T}$.)

768. **$AgNO_3$** gives a white precipitate, which becomes grey when it is heated. Solution of citrate, if it is gently heated with ammoniacal $AgNO_3$-solution, causes either very slight precipitation of Ag or none at all (758). (Difference from tartrate.)

3. AROMATIC ACID-RADICLES.

The Aromatic Acid-radicles included here are benzoate, salicylate, gallate, tannate, and hippurate. Meconate and urate are also included in this section.

BENZOATE, $(C_7H_5O_2)'$.—Use Ammonium benzoate, $AmC_7H_5O_2$.

Benzoic acid and benzoates commonly emit an aromatic smell of gum benzoin, from which they have been usually prepared.

769. Benzoic acid, $C_6H_5.COOH$, usually crystallises in lustrous flat plates, which melt at 121° and boil at 249° C. It is sparingly soluble in cold water, more soluble in hot water, and readily soluble in alcohol, in ether and in chloroform.

Owing to its slight solubility in cold water the acid is partially precipitated from its solution in alcohol when water is added, or when strong HCl or any other strong acid is added to an aqueous solution of a benzoate.

Most of the benzoates are soluble in water.

770. **Ignition.**—When benzoic acid is heated, it fuses and evolves dense white fumes, which cause coughing when they are inhaled.

Benzoates give off benzene when they are heated with soda-lime: the benzene is recognised by its smell and by burning with a smoky flame, and by the properties described in paragraphs 814 and 815.

771. **Mineral acids** throw down a white crystalline precipitate of benzoic acid, when they are added to the aqueous solution of a benzoate.

772. **Ethyl benzoate test.**—If one c.c .of strong H_2SO_4 and an equal volume of alcohol are poured upon benzoic acid or a benzoate, and the mixture is warmed, a fragrant smell of ethyl benzoate will be perceived.

773. **$FeCl_3$** gives a buff-coloured precipitate of basic ferric benzoate which is soluble in AmOH. If this precipitate is heated with strong HCl, benzoic acid separates in crystalline plates. (Difference from succinate.)

774. **$AgNO_3$**, white precipitate, $AgC_7H_5O_2$, soluble in hot water, from which it recrystallises on cooling.

775. **Reduction.**—If a little dilute H_2SO_4 and a few pieces of magnesium wire are added to a solution of a benzoate, a fragrant smell of benzaldehyde, C_6H_5COH, will be perceived.

SALICYLATE, $(C_7H_5O_3)'$.—Use Sodium salicylate, $NaC_7H_5O_3$.

776. Salicylic acid, $C_6H_4.OH.COOH$, forms colourless, needle-shaped crystals. The ortho-acid melts at 156·5°, and at a somewhat higher temperature it decomposes into CO_2 and phenol or carbolic acid, $C_6H_5.OH$. It is sparingly soluble in cold water, but more soluble in hot water; it is readily soluble in alcohol and in ether.

777. **Ignition with Soda-lime.**—The decomposition of salicylic acid by heat is rapid and complete, if the acid has been mixed with excess of soda-lime before it is heated; phenol is produced and condenses as a white crystalline sublimate in the cooler part of the tube (848).

778. **Dilute mineral acids** decompose salicylates and cause the separation of white needle-shaped crystals of salicylic acid.

779. **$FeCl_3$.**—When $FeCl_3$ is added to solution of salicylic acid it becomes *violet*: the colour is destroyed by HCl, but not by HĀ. (Difference from phenol.)

780. **Heated with H_2SO_4 and Methyl alcohol,** salicylate gives a fragrant smell of methyl salicylate, or "oil of winter-green."

781. **H_2SO_4 and Nitrite.**—The addition to salicylate of strong H_2SO_4, which has been mixed with a small quantity of 6 per cent. aqueous solution of KNO_2, causes a *permanent* red coloration. (Difference from phenol.)

782. **Bromine-water** gives a white precipitate of tribrom-salicylic acid.

GALLATE, $(C_7H_5O_5)'$.—Use Gallic acid, $H.C_7H_5O_5$.

783. Gallic acid, $C_6H_2(OH)_3.COOH$, forms yellowish acicular crystals containing one molecule of water. It is slightly soluble in cold water, readily soluble in hot water, in alcohol and in glycerol, and sparingly soluble in ether.

784. **Ignition.**—When gallic acid is heated, it gives off water at 120° C., melts at about 210° C., and at 253° CO_2 is evolved and pyrogallol (859) sublimes.

785. **Strong H_2SO_4,** when it is heated with gallic acid or a gallate, gives a green solution which changes colour to purple, and SO_2 is eventually evolved.

786. **$FeCl_3$ solution** yields a *bluish-black* precipitate which is soluble in excess to a green solution.

787. **KCN solution,** if it is freshly made, gives a red coloration which rapidly disappears, but the colour reappears when the liquid is shaken up with the air. (Distinction from tannate.)

788. **Reducing action :** when Fehling-solution (909) is warmed with gallic acid, it is gradually reduced with separation of red cuprous oxide. Silver solutions are also reduced by gallic acid with separation of black metallic silver.

TANNATE.—Use tannic acid, $C_{14}H_{10}O_9$.

789. Tannic acid in the pure state is a colourless powder, but the commercial acid usually has a yellowish tint. It has a very astringent taste, and is readily soluble in water and in dilute alcohol, but is almost insoluble in absolute alcohol and in ether. It is precipitated when acid is added to its aqueous solution.

790. **Ignition.**—When tannic acid is heated in a tube it blackens, and gives off H_2O, CO_2 and pyrogallol; the pyrogallol condenses in yellowish drops, which crystallise as they cool.

791. **Strong H_2SO_4,** when it is heated with a tannate, gives a brown coloration, and SO_2 is eventually evolved. (Difference from gallate.)

792. **$FeCl_3$** gives a bluish-black precipitate, which is the colouring substance of one of the common inks.

793. **PbN_2O_6 :** white precipitate of lead tannate. (Distinction from gallate and pyrogallol.)

794. **KCN solution** gives a reddish-brown coloration.

795. **NaOH** dissolves tannic acid, and the solution turns brown in the air by undergoing oxidation.

796. **Gelatine** is precipitated from its solution by tannic acid. (Difference from gallic acid.)

HIPPURATE, $(C_9H_8NO_3)'$.—Dissolve Hippuric acid, $H.C_9H_8NO_3$, in very dilute AmOH-solution, and neutralise when necessary.

797. Hippuric acid, $C_6H_5.CO.NH.CH_2.COOH$, occurs in colourless prismatic crystals: it has a bitter taste and a strongly acid reaction: it is only slightly soluble in cold water, but is freely soluble in hot water and in alcohol. The acid melts at 189° C.

798. **Ignition with Soda-lime.**—When a solid hippurate is heated with soda-lime, it evolves NH_3 and benzene, C_6H_6 (814).

799. **HCl** produces a white crystalline precipitate of hippuric acid in a neutral solution of a hippurate.

800. **$FeCl_3$** causes a flesh-coloured precipitate: this is decomposed by HCl with separation of crystalline needles of hippuric acid.

MECONATE, $(C_7H_2O_7)''$.—Use solution of Meconic acid, $H_2C_7H_2O_7.3H_2O$, neutralising it with dilute AmOH.

801. Meconic acid, $C_5HO_2.OH(COOH)_2$, is present as morphine meconate in opium and in opium extract. It forms colourless crystalline scales, which are slightly soluble in cold water, and readily soluble in hot water and in alcohol.

802. **Ignition.**—When meconic acid is heated in a tube to 100° C. it loses its water of crystallisation, and at 120° C. it forms CO_2 and comenic acid; at a higher temperature it chars and emits the odour of caramel.

803. **$FeCl_3$.**—Meconic acid may be detected by the production of a purple-brown coloration when it is mixed with $FeCl_3$-solution. When this liquid is boiled, a precipitate of basic ferric meconate is precipitated, as is the case with ferric acetate or formate.

804. **PbA_2 solution** gives in solution of a meconate a pale-yellow precipitate of lead meconate, which is insoluble in $H\bar{A}$ but soluble in dilute HNO_3.

805. **$CaCl_2$ solution** gives in neutral solution of a meconate a white precipitate of $CaC_7H_2O_7$.

806. **$AgNO_3$** gives in a strong solution of meconate a white precipitate of $Ag_2C_7H_2O_7$, which changes to bright yellow when a drop of AmOH is added.

URATE, $(C_5H_3N_4O_3)'$.—Use Potassium urate, $KC_5H_3N_4O_3$.

807. Uric acid, $C_5H_4N_4O_3$, is a white crystalline powder, which is almost insoluble in cold and hot water, and is insoluble in alcohol and in ether.

808. **Ignition.**—When a urate is heated in an ignition-tube it chars and evolves NH_3, HCNO and HCN. If it has been mixed with NaOH or with soda-lime before being heated, NH_3 is evolved and NaCN is left in the solid residue.

809. **HNO_3** dissolves the acid with effervescence: if this solution is evaporated to dryness in a porcelain dish, and the residue is then moistened with AmOH, unless AmOH was originally present, bright red *murexide* is formed; this becomes purple when KOH is added.

810. **HCl** precipitates white uric acid from solution of a urate.

GROUP II.—HYDROCARBONS AND THEIR DERIVATIVES.

The substances included under this heading are turpentine, benzene, naphthalene, anthracene, chloroform, carbon tetrachloride, iodoform and carbon disulphide.

TURPENTINE, $C_{10}H_{16}$.

811. Turpentine is a mixture of a number of isomeric liquids which have the formula $C_{10}H_{16}$, pinene being the constituent which is present in largest proportion. Turpentine possesses a characteristic smell; it boils at 160° C., and its density is 0·876. The warm liquid is easily kindled, and burns with a very smoky flame. It is not miscible with water, but readily dissolves in strong alcohol and in ether.

812. **Strong H_2SO_4,** when it is mixed in small quantity with turpentine, causes a peculiar and very characteristic smell to be evolved when the mixture is warmed.

813. **Br-water,** when it is shaken up with turpentine, is at once decolorised.

BENZENE, C_6H_6.

814. Benzene is a very mobile, volatile, strongly smelling liquid which burns readily with a smoky flame. It boils at 80° C., and its specific gravity is 0·8839. It is miscible with alcohol and with ether, but is insoluble in water.

815. **HNO_3.**—If strong fuming nitric acid, or a mixture of strong H_2SO_4 and strong HNO_3, is warmed with benzene, nitrobenzene, $C_6H_5NO_2$, is produced: and this substance separates as a reddish-yellow oil, smelling of bitter almonds, when the acid liquid is largely diluted with water.

If this nitro-benzene is poured into dilute HCl and pieces of zinc are introduced, aniline is formed and may be detected by the tests in paragraphs 980–982.

NAPHTHALENE, $C_{10}H_8$.

816. Naphthalene crystallises in shining plates, which melt at 80° C., and when further heated boil at 218° C. Naphthalene is insoluble in water, but is readily soluble in hot alcohol and in ether. It possesses a characteristic smell and is very volatile, the vapour

burning with a bright smoky flame. Naphthalene vapour is always present in coal-gas, and contributes largely to the illuminating power of the gas.

ANTHRACENE, $C_{14}H_{10}$.

817. Anthracene crystallises in colourless glistening leaflets, which show a fine blue fluorescence. It melts at 216·6°, and boils at 351° C. It dissolves readily in hot benzene, but sparingly in alcohol and in ether.

CHLOROFORM, $CHCl_3$.

818. Chloroform is a colourless, mobile liquid, with an ethereal smell and sweetish taste, which boils at 61·2°, and has a density of 1·5. It is only slightly soluble in water, but is miscible with alcohol and with ether. Its vapour, when inhaled, acts as a powerful anæsthetic.

819. **Formation of Phenyl isocyanide.**—When chloroform is mixed with a drop of aniline, and with some alcoholic solution of KOH, and the mixture is heated, an *intensely disagreeable* smell of phenyl isocyanide is given off.

820. **Fehling's-solution** (909), when it is warmed with chloroform, deposits red cuprous oxide after some time.

821. **Phenol and KOH.**—If a mixture of alcoholic solution of phenol with KOH is evaporated to dryness on the water-bath, the residue assumes a beautiful purple colour when it is moistened with chloroform. (Difference from chloral.)

CARBON TETRACHLORIDE, CCl_4.

822. Carbon tetrachloride is a mobile liquid, with a boiling-point of 76·7° and a density of 1·6. It is insoluble in water but miscible with alcohol and with ether.

823. **Phenyl isocyanide test.**—When carbon tetrachloride is heated with a drop of aniline and with alcoholic potash, the nauseous smell of phenyl isocyanide is produced, but more slowly than with chloroform (819).

IODOFORM, CHI_3.

824. Iodoform is a bright yellow substance, which emits a characteristic smell, and crystallises in hexagonal plates or stars. It

has a density of 4·01, melts at 119° C., and when further heated it vaporises and evolves iodine and HI, leaving a residue of carbon. It is insoluble in water and in acids, but dissolves in alcohol and in ether.

When it is boiled with KOH-solution, iodoform breaks up into a mixture of potassium formate and potassium iodide, which may be separately identified (728–730 and 552–556).

When iodoform is warmed with solution of phenol in alcoholic NaOH, a red coloration is produced.

CARBON DISULPHIDE, CS_2.

825. Carbon disulphide is a mobile, highly refractive liquid. When it is pure it possesses a pleasant ethereal smell; but it usually emits an extremely repulsive odour, which is due to the presence of impurity. It boils at 46° C., and has a density of 1·292. It is not miscible with water, but dissolves in alcohol and in ether; it readily dissolves fatty bodies and oils. CS_2 is volatile, and the vapour is readily kindled, burning with a blue flame and producing SO_2 and CO_2.

826. **Formation of Potassium xanthate.**—If CS_2 is heated with alcoholic solution of KOH, potassium xanthate, $CS.OC_2H_5.SK$, is formed: the addition of $CuSO_4$-solution to this liquid produces a *yellow precipitate* of copper xanthate.

827. **KOH**, when it is boiled with CS_2, forms a brown solution containing K_2CO_3 and K_2CS_3: on the addition of one drop of $Pb\bar{A}_2$-solution, black PbS is precipitated.

NITROBENZENE, $C_6H_5NO_2$.

828. Nitrobenzene is a pale-yellow liquid, smelling of bitter almonds: its density is 1·187, and it boils at 210·9°: it is insoluble in water, but is miscible with most organic liquids.

829. **Reduction to aniline**: if a little nitrobenzene is mixed with dilute HCl and a few small pieces of zinc are introduced, aniline is gradually formed, and may be detected as is described in paragraphs 980–982.

GROUP III.—ALCOHOLS AND ETHERS.

In this Group there are included methyl alcohol, ethyl alcohol, amyl alcohol, glycerol, ethyl ether and ethyl acetate.

METHYL ALCOHOL, $CH_3.OH$.

830. **Methyl alcohol** resembles ethyl alcohol (834) in its general properties. It boils at 64·7° C., and has a density of 0·81. It is miscible with water and with ether in all proportions. Its vapour, when it is kindled, burns with a pale blue flame.

831. **Oxidation to Formic acid.**—If a mixture of methyl alcohol with dilute H_2SO_4 and $K_2Cr_2O_7$ is distilled (32, 672), the distillate will contain formic acid; and when this *acid distillate* is warmed with $AgNO_3$, it will cause a brilliant silver mirror to be deposited.

When ethyl alcohol is oxidised by similar treatment, it yields aldehyde, and this only deposits a silver mirror when it is warmed with $AgNO_3$ *in an alkaline solution* (879).

832. **Formation of Methyl salicylate.**—When methyl alcohol is heated with strong H_2SO_4 and salicylic acid, a fragrant smell of methyl salicylate, or "oil of winter-green," is evolved.

833. **Iodoform** is not produced when pure methyl alcohol is warmed with excess of iodine in the presence of Na_2CO_3 (836). (Difference from ethyl alcohol.)

ETHYL ALCOHOL, $C_2H_5.OH$.—Use rectified spirit diluted with four times its volume of water.

834. **Ethyl alcohol** is a mobile fragrant liquid: it boils at 78°, has a density of 0·7937 at 15° C., and its vapour burns with a pale blue smokeless flame. It is miscible in all proportions with water and with ether.

If much water is prese. ' with the alcohol, it may be necessary to add dry K_2CO_3 in excess to the liquid, and then to distil over about one-third of it (32, 672). The alcohol is thus concentrated, and is much more readily detected by the following tests in the distillate than in the original dilute liquid.

835. **Strong H_2SO_4,** when it is mixed with alcohol and heated, gives off ether and ethylene, which burn with a *luminous* flame.

836. **Formation of Iodoform.**—If Na_2CO_3-solution is added to water which contains a little alcohol, and the mixture is gently

heated for some time, small pieces of iodine being occasionally added until the solution retains a brown colour, *golden yellow crystals of iodoform* will separate. If very little alcohol was present, the liquid may require to stand for ten or twelve hours before the crystals make their appearance.

When these crystals are examined under the microscope, they are seen to be hexagonal tablets or six-pointed stars.

This reaction is yielded by other substances, such as aldehyde, acetone and ethyl acetate, and is therefore not altogether characteristic of ethyl alcohol.

837. **Formation of Aldehyde and Acetic acid.**—Alcohol may be converted by oxidation into aldehyde and acetic acid, by heating it for some time with $K_2Cr_2O_7$ and H_2SO_4. During the process of oxidation, aldehyde will be first smelt, and then acetic acid.

If the smell is not distinctly recognised, the liquid may be distilled and the first portion of the distillate divided into two portions: one portion may then be tested for aldehyde by paragraph 880, and the other may be neutralised with Na_2CO_3, evaporated to dryness, and the solid residue tested for acetate (733–737).

It must be remembered that acetic acid may result from the oxidation of other substances besides alcohol.

838. **Benzoic- and Acetic-ether.**—When ethyl alcohol is heated with strong H_2SO_4 and a benzoate or an acetate, the characteristic smell of ethyl benzoate or of ethyl acetate will be recognised.

AMYL ALCOHOL, $C_5H_{11}.OH$.

839. The commercial alcohol is isoamyl alcohol; it is a colourless oily liquid, and its vapour has a strong smell and causes coughing when it is inhaled. The alcohol is only slightly soluble in water; it boils at 131·6° C., and has a density of 0·82.

840. **Strong H_2SO_4,** when it is warmed with amyl alcohol, gives a reddish-brown coloration: if a few drops of glacial acetic acid and one c.c. of $FeCl_3$-solution are then added, a purple colour is produced in the warm liquid.

841. **Sodium acetate,** if it is added together with a little dilute H_2SO_4 and warmed, gives a pear-like odour, which is due to the formation of amyl acetate.

GLYCEROL, OR GLYCERINE, $C_3H_5(OH)_3$.

842. Glycerol is a colourless, hygroscopic, viscous liquid, with an intensely sweet taste. It has a density of 1·27, a melting point

of 20° C., and a boiling-point of 290°. It burns with a somewhat luminous flame, and is miscible with water and with alcohol, but not with ether.

843. **$NaHSO_4$.**—When glycerine is heated with $NaHSO_4$, it evolves intensely pungent acrolein vapour. If this vapour is passed into solution of rosaniline, which has been previously decolorised by SO_2, it produces a red coloration. Other aldehydes produce a similar coloration.

844. **Phenol and H_2SO_4.**—If phenol, strong sulphuric acid and glycerine are mixed together in equal volumes, and the mixture is heated to 120° C., and is then diluted and mixed with excess of AmOH, it becomes *crimson* in colour.

ETHYL ETHER, $(C_2H_5)_2O$.

845. Ether is a very mobile, volatile, fragrant liquid, which is easily kindled and burns with a bright flame. It has a boiling-point of 34·6° C., and a density of 0·7201. Ether dissolves in about ten times its volume of water, and is miscible with alcohol and with other organic liquids.

ETHYL ACETATE, OR ACETIC ETHER, $C_2H_5.C_2H_3O_2$.

846. Ethyl acetate, $CH_3.COOC_2H_5$, is a very mobile, fragrant liquid. It has a boiling-point of 77·2° C., and a density of 0·9048: it is somewhat soluble in water, and is readily soluble in alcohol.

847. **KOH.**—Acetic ether is hydrolysed by KOH in a manner which is typical of similar organic bodies :—

$$C_2H_5.C_2H_3O_2 + KOH = C_2H_5.OH + KC_2H_3O_2.$$

This change may be effected by simply warming the liquid for some time with KOH.

When the resulting liquid is distilled, alcohol may be detected in the distillate (836), and acetate may be found in the distillation flask (733–737).

GROUP IV.—PHENOL AND ITS DERIVATIVES.

PHENOL, OR CARBOLIC ACID, $C_6H_5.OH$.—Use solution of a small crystal of the substance in hot water.

848. **Phenol** is a colourless crystalline substance; the commercial substance, however, usually has a pinkish tinge. Its smell is very characteristic. It melts at 43° C. and boils at 181° C., and has a density of 1·05. It is slightly soluble in water, but freely soluble in benzene, in alcohol and in ether. It is also soluble in caustic alkali solution, but insoluble in solution of alkaline carbonate. (Distinction from the true acids.)

849. **$FeCl_3$ solution** gives with phenol solution a violet coloration, which is destroyed by HĀ.

850. **Bromine-water,** or **Bleaching-powder** solution, when it is added to phenol solution, which has been previously mixed with a quarter of its volume of dilute AmOH, produces a blue coloration: this colour changes to red when an acid is added.

851. **Liebermann's reaction.**—If a crystal of KNO_2 is dissolved in strong H_2SO_4 and the solution is added to phenol, a green coloration is produced, or a brown coloration if sufficient acid is not present. If this solution is then poured into water a red coloration is produced, and this changes back to green when the liquid is made alkaline by adding NaOH.

852. **Bromine water,** when it is added to phenol solution, gives a pale yellow precipitate of tribromphenol bromide, $C_6H_2Br_3.Br$.

853. **Strong HNO_3,** where it is warmed with a little phenol solution, gives a bright yellow liquid containing picric acid: the colour of this solution is made more intense by adding NaOH. If this solution is boiled with a little glucose its colour changes to deep red, owing to the formation of picraminic acid.

HYDROQUINONE, $C_6H_4(OH)_2$.

854. Hydroquinone is a white crystalline substance which shows a greenish tint. It melts at 170·3°, boils at 285° C., and is soluble in water, in alcohol, and in ether, but is insoluble in benzene.

855. **$FeCl_3$,** if it is added to a dilute solution of hydroquinone, gives a green coloration which rapidly changes to reddish-brown. If $FeCl_3$ is added to a strong solution, or to solid hydroquinone, a dark green crystalline precipitate is formed.

856. **$AgNO_3$ solution** is reduced by hydroquinone solution, and metallic Ag is precipitated.

857. **KOH solution** becomes brown when it is shaken with hydroquinone solution.

858. **$KMnO_4$ solution** acidified with dilute H_2SO_4, when it is boiled with hydroquinone solution, evolves the irritating odour of quinone.

PYROGALLOL, OR PYROGALLIC ACID, $C_6H_3(OH)_3$.

859. Pyrogallol is a white crystalline substance: it melts at 132° C., boils at 293°, and is readily soluble in water, in alcohol and in ether, but is less soluble in chloroform and in benzene.

860. **KOH** and other caustic alkalis readily dissolve this substance, and the solutions rapidly become brown by absorption of oxygen from the air.

861. **$FeSO_4$** colours pyrogallol solution dark blue.

862. **$FeCl_3$** gives a green coloration to pyrogallol solution.

863. **$AgNO_3$** is immediately reduced by pyrogallol solution, and metallic silver is precipitated.

864. **$Ca(OH)_2$** gives a purple coloration which changes to brown.

865. **Fehling's solution** (909) is reduced when it is heated with pyrogallol solution, and red Cu_2O is precipitated.

TRINITROPHENOL, OR PICRIC ACID, $C_6H_2(NO_3)_3.OH$.

866. Picric acid is a yellow crystalline substance, which melts at 122·5°C. Its taste is intensely bitter and it stains the skin yellow. It is very slightly soluble in cold water, but is readily soluble in hot water, in alcohol, and in ether. The metallic picrates undergo violent explosive decomposition when they are placed under suitable conditions.

867. **Ignition:** picric acid fuses when it is heated in an ignition-tube, and then explodes slightly, giving off dense black fumes.

868. **Bleaching-powder** solution, when it is heated with picric acid, gives off the pungent odour of chlorpicrin, which resembles that of mustard-oil.

869. **KOH and Glucose,** when they are heated with picric acid, yield an intense red colour, which is due to the formation of picraminic acid.

870. **Ammonia-copper sulphate solution,** made alkaline with AmOH, gives a bright green precipitate.

871. **NaOH dissolved in alcohol** gives a deep yellow precipitate of sodium picrate, $C_6H_2(NO_3)_3ONa$.

GROUP V.—ALDEHYDES AND KETONES.

FORMALDEHYDE, H.COH.—Use "formalin" liquid.

872. Formaldehyde is a gas with a peculiar pungent smell. Commercial "formalin" is a 40 per cent. solution of formaldehyde

in water. When the aqueous solution of formaldehyde is evaporated on the water-bath, white solid paraformaldehyde is produced.

873. **Ammoniacal silver nitrate** (879), when it is mixed in a test-tube with a little formaldehyde, and the mixture is warmed by placing the tube in a beaker of hot water, yields a brilliant silver coating on the inside of the test-tube :—$H.COH + Ag_2O = H.COOH + Ag_2$.

874. **Fehling's solution** (909) is reduced when it is warmed with formaldehyde, and red cuprous oxide is precipitated. (Aromatic aldehydes do not reduce Fehling's solution.)

875. **Schiff's reaction.**—If formaldehyde is added to a dilute solution of magenta (fuchsine), which has been previously decolorised by means of sulphurous acid, the solution will gradually become pink and ultimately magenta in colour.

876. **Pyrogallol** in freshly prepared solution, if it is added to formaldehyde and the mixture is then acidified with *strong* HCl, yields gradually a white precipitate which eventually changes in colour to deep red.

877. **Phenylhydrazine hydrochloride solution,** if it is mixed with an equal volume of dilute sodium nitroprusside solution, and is then added to a little dilute formaldehyde solution and rendered alkaline with NaOH, gives an intense blue coloration.

ACETALDEHYDE, $CH_3.COH$.

878. Acetaldehyde is a very mobile liquid, possessing a most characteristic smell : it boils at 20·8° C., and has a density of 0·778, unless it is partially polymerised. It is miscible with water, with alcohol and with ether in all proportions.

879. **$AgNO_3$ solution,** if it is mixed with very dilute AmOH until the precipitate which forms at first just disappears, and is then heated with acetaldehyde, produces a silver mirror on the glass. The test is made as is directed in paragraph 759.

880. **Schiff's reaction.**—Magenta (fuchsine) solution, which has been decolorised by SO_2, produces a violet-red colour when it is mixed with acetaldehyde.

881. **KOH solution,** when it is heated with acetaldehyde, produces aldehyde-resin, a yellow substance with a peculiar smell.

882. **H_2S,** when it is passed into the aqueous solution of alde-

hyde, produces an oily liquid, which is changed by acids into a solid polymer.

883. **$NaHSO_3$,** in saturated solution, gives a crystalline precipitate ($C_2H_4O.NaHSO_3$), which is decomposed by acids and by alkalis with liberation of aldehyde. This reaction is common to many aldehydes.

884. **Pyrogallol and strong HCl** (876) give with acetaldehyde a white precipitate, which gradually turns yellow. With a dilute solution the precipitate only appears after a time.

CHLORAL, $CCl_3.COH$.—Use Chloral hydrate, $CCl_3.CH(OH)_2$, dissolved in water.

885. Chloral is a colourless liquid, with a pungent tear-exciting smell: it boils at 97·7°, and has a density of 1·512. It unites with water, forming crystalline chloral hydrate, which melts at 47·4°, boils at 97·5°, and has a density of 1·58. Choral readily dissolves in water, in alcohol and in ether.

886. **Phenyl isocyanide test.**—When chloral hydrate is heated with alcoholic solution of KOH and aniline, it yields phenyl isocyanide, which is recognised by its extremely offensive smell (819).

887. **Silver mirror.**—When chloral hydrate is warmed in a test-tube with ammoniacal $AgNO_3$-solution (759) and a drop of KOH solution, a silver mirror is readily deposited on the inside of the tube. (Difference from chloroform.)

888. **Fehling's solution** (909) is reduced when it is warmed with chloral hydrate, and red Cu_2O is formed.

889. **Schiff's reaction.**—Chloral gives the magenta reaction (875), whereas chloral hydrate does not.

890. **KOH.**—Chloral hydrate is decomposed by aqueous KOH solution: chloroform separates in minute drops, and potassium formate remains in solution.

BENZALDEHYDE, $C_6H_5.COH$.

891. Benzaldehyde is a colourless and highly refractive liquid with a fragrant smell: it has a density of 1·05, and boils at 179° C.: it is sparingly soluble in water, but readily soluble in alcohol and in ether. On exposure to the air it is slowly converted into benzoic acid (769 *et seq.*).

892. **KOH**: when benzaldehyde is heated with solid KOH, benzyl alcohol and potassium benzoate are formed; and if the resulting solution is acidified with HCl, benzoic acid is precipitated (771).

893. **$AgNO_3$** in ammoniacal solution is reduced by this aldehyde to metallic silver.

894. **Na_2SO_3 solution** dissolves benzaldehyde: the careful addition of dilute H_2SO_4 to this solution precipitates crystalline flocks of $C_7H_6O.NaHSO_3$.

Schiff's reaction (875) is given by benzaldehyde.

ACETONE, OR DIMETHYL-KETONE, $CO(CH_3)_2$.

895. Acetone is a mobile liquid, with a peculiar and characteristic smell: it boils at 56·1° C., and has a density of 0·7965: it is miscible with water, alcohol and ether in all proportions.

896. **Iodoform reaction**: if a few drops of solution of iodine in KI-solution are mixed with solution of acetone, and Na_2CO_3-solution is then added until the brown colour of the mixture disappears, and the liquid is warmed, iodoform will separate in golden yellow plates as the liquid cools.

This reaction is also given by ethyl alcohol.

If, however, a solution of acetone is made alkaline with AmOH and a solution of I in KI-solution is added drop by drop, a black precipitate of nitrogen iodide will form: this black precipitate will disappear when the liquid is gently warmed, and iodoform will then crystallise out when the liquid is cooled. Ethyl alcohol does not yield iodoform under these conditions.

897. **$HgCl_2$ solution**, if it is made strongly alkaline by alcoholic solution of KOH, yields a precipitate of HgO: when the liquid containing the precipitate is shaken with acetone, part of the HgO is dissolved; if the liquid is then filtered, Hg may be shown to be present in the filtrate either by adding Am_2S (134), or by acidifying the liquid with HCl and adding $SnCl_2$ (135).

898. **Sodium nitroprusside**, if it is added to acetone solution which has been previously mixed with twice its volume of strong NaOH-solution, produces a *bright red* coloration: this coloration becomes bluish when HĀ is added.

899. **$NaHSO_3$**, in saturated solution, gives a crystalline precipitate ($C_3H_6O.NaHSO_3$), which is decomposed by acid or alkali with liberation of acetone.

900. **Parabromphenylhydrazine**, if it is dissolved in glacial acetic acid and is then diluted and mixed with acetone, gradually yields yellowish needles of bromphenyl hydrazone.

GROUP VI.—CARBOHYDRATES.

901. The general name of carbohydrate has been given to those compounds of carbon, hydrogen and oxygen which contain hydrogen and oxygen in the atomic relation of $H_{2n}O_n$, that is in the proportion in which these elements are present in water.

This Section gives the reactions of the sugars; and includes the glucoses, dextrose and levulose ($C_6H_{12}O_6$); and the saccharoses, sucrose, maltose and lactose ($C_{12}H_{22}O_{11}$). The reactions of carbohydrates of the general formula $(C_6H_{10}O_5)_n$, including cellulose, starch and dextrin, are also given.

GENERAL REACTION FOR THE SUGARS.

902. When a sugar, which contains an aldehydic group (COH) or a ketonic group (CO), is heated with one molecule of phenyl hydrazine, it is converted into a hydrazone: thus glucose forms glucose phenyl hydrazone:—

$$\underset{\text{Glucose.}}{CH_2(OH)(CH.OH)_4COH} + \underset{\text{Phenyl hydrazine.}}{C_6H_5NH.NH_2} =$$

$$\underset{\text{Glucose phenyl hydrazone.}}{CH_2(OH)(CH.OH)_4CH : N.NHC_6H_5} + H_2O$$

If an excess of phenyl hydrazine is added, the final CHOH group is oxidised to CO, and part of the phenyl hydrazine is reduced to aniline and NH_3:—$C_6H_5NH.NH_2 + H_2 = C_6H_5NH_2 + NH_3$.

The oxidation product of the phenyl hydrazine then combines with a second molecule of phenyl hydrazine and yields an osazone:—

$$CH_2(OH)(CH.OH)_3CO.CH : N.NH.C_6H_5 + C_6H_5.NH.NH_2 =$$

$$\underset{\text{Osazone.}}{CH_2(OH)(CHOH)_3 : C(N.NHC_6H_5).CH : N.NH.C_6H_5} + H_2O$$

The melting-point of the osazone is characteristic of the sugar from which it has been derived. Hence the preparation of an osazone (903) is often carried out in order to identify a sugar.

903. Preparation of Osazones.—Dissolve half a gramme of the sugar in 5 c.c. of water in a test-tube, add 3 c.c. of phenyl hydrazine and then 3 c.c. of acetic acid, and place the test-tube in boiling water for about ten minutes. The osazone will separate in yellow crystals, which are filtered off, washed with water, and dried. Their melting-point is then determined (669, 670).

DEXTROSE, DEXTRO-GLUCOSE, OR GRAPE SUGAR, $C_6H_{12}O_6$.

904. Dextrose is a colourless soluble solid, with a sweet taste. It crystallises from its solution in alcohol in the anhydrous state,

and these crystals fuse at 146°C.: from its solution in water it crystallises in a hydrated form, $C_6H_{12}O_6.H_2O$, which melts at 86°C. Dextrose is readily soluble in water and in dilute alcohol, but is insoluble in strong alcohol and in ether. Its density is 1·55, and its specific rotatory power is $[\alpha]_D + 52{\cdot}8$°C. Dextrose can be fermented by yeast. Its osazone melts at 204°.

905. **Ignition.**—When glucose is heated in an ignition-tube, it melts at about 86°C., becomes anhydrous at 146°C., and turns brown at higher temperatures giving off the characteristic smell of burnt sugar.

906. **Strong H_2SO_4.**—Dextrose is distinguished from other sugars, by yielding only a *yellow liquid* when strong H_2SO_4 is added to its strong solution, and the mixture is kept cool. (Distinction from cane-sugar.)

When this yellow liquid is heated, it blackens.

907. **KOH.**—When dextrose is warmed with strong KOH-solution, the liquid becomes *brown*. (Distinction from cane-sugar.)

908. **Reduction of CuO.**—If a few drops of $CuSO_4$-solution are mixed with dextrose-solution, and excess of KOH-solution is then added, no precipitate is formed; but when this mixture is heated, yellow cuprous hydroxide is formed, and this is converted into red Cu_2O when the liquid is more strongly heated.

The dextrose solution may be advantageously mixed with Fehling-solution (909) in this test, instead of being mixed with $CuSO_4$ and KOH.

909. **Fehling solution** is prepared as follows: 35 grammes of crystallised $CuSO_4.5H_2O$ are dissolved in one litre of water, and the clear solution is kept in a stoppered bottle. 173 grammes of Rochelle-salt ($KNa\bar{T}$), and sixty grammes of NaOH are then dissolved in a litre of water; this solution is kept in a corked bottle. Equal volumes of these two solutions are mixed together in order to prepare the Fehling-solution.

910. **Silver mirror.**—If dextrose is gently heated with ammoniacal $AgNO_3$-solution (759, *Note*) in a glass vessel, a silver mirror will be produced on the interior of the glass.

911. **Other Reduction tests.**—Dextrose differs from maltose and lactose by forming red Cu_2O when it is boiled with $Cu\bar{A}_2$-solution containing $H\bar{A}$. When dextrose is mixed with solutions of KOH and of basic bismuth nitrate and heated, it yields a black precipitate.

912. **Picric acid.**—If dextrose is boiled with KOH-solution and a little picric acid a yellow colour is produced, which

changes to deep red: the colour is due to the formation of picraminic acid.

913. **Fermentation.**—If clean freshly-washed *yeast* is added to dextrose-solution in the flask shown in Fig. 56, page 135, and the temperature of the liquid is maintained at about 25°C. for an hour or more, fermentation will take place with the production of ethyl alcohol and carbon dioxide gas.

The escaping gas may be shown to be CO_2 by letting it bubble through lime-water (474, 4), and ethyl alcohol may be found in the liquid which remains in the flask by the reactions in paragraphs 836, 837.

This reaction by fermentation is given by other sugars.

914. **Osazone.**—When dextrose is heated with phenyl hydrazine and acetic acid (903) yellow crystals of the osazone are formed, which melt at 204°C.

915. **Lead acetate,** if it is added to glucose solution and the liquid is boiled, then mixed with AmOH in quantity just sufficient to produce a white precipitate and further boiled, yields a pink precipitate. (Difference from sucrose and lactose.)

LEVULOSE, OR FRUCTOSE, $C_6H_{12}O_6$.

916. Levulose is usually a colourless, difficultly crystallisable syrup. It is sweeter than dextrose, and is also more soluble in water and in alcohol. Its specific rotatory power is $[\alpha]_D - 102° - 0{\cdot}56.t°$, and its melting-point is 95°C. It can be fermented by yeast, but differs from dextrose by forming an insoluble compound with lime. Its osazone (903) melts at 204°C.

SUCROSE, OR CANE-SUGAR, $C_{12}H_{22}O_{11}$.

917. Cane-sugar is a colourless crystalline substance, which is easily soluble in water and is intensely sweet in taste. It is only sparingly soluble in alcohol. Cane-sugar fuses at 160°C, and is readily charred by heat. Its density is 1·59, and its specific rotatory power is $[\alpha]_D + 66{\cdot}5°$. It is not readily fermented by yeast, and it does not form an osazone.

918. **Strong H_2SO_4** produces a deep brown coloration if the mixture is kept cool; but the liquid ultimately becomes black owing to the separation of carbon. (Difference from other sugars.)

The presence of much water prevents this change from occurring at ordinary temperatures, but the liquid darkens when it is heated.

919. **KOH** produces no coloration (907), and neither silver solution nor alkaline copper-solution is reduced (910, 912). (Difference from dextrose, maltose and lactose.)

920. **Conversion into Glucose.**—Sucrose solution, when it is heated for a minute with a few drops of strong HCl, yields a mixture of equal quantities of dextrose and levulose which is known as "invert sugar." After this acid sugar-solution has been neutralised by KOH, it reduces Fehling-solution (909).

921. **Citric acid,** in 5 per cent. solution, when it is boiled with sucrose also hydrolyses it and forms glucoses. (Distinction from maltose and lactose.)

922. Cane-sugar may be identified in the presence of dextrose, maltose and lactose by its inability to reduce Fehling-solution (909).

If a solution which contains these sugars is mixed with Fehling-solution and heated on a water-bath until no further reduction takes place, as is shown by the blue colour of the liquid remaining, any sugar still in solution will be sucrose. The precipitated Cu_2O may be filtered off and the filtrate acidified with dilute H_2SO_4 and boiled for five minutes, then rendered alkaline with NaOH and again heated with Fehling-solution: reduction and separation of Cu_2O will take place if cane-sugar was present since it has been converted into "invert sugar" by being heated with the acid (920).

MALTOSE, OR MALT-SUGAR, $C_{12}H_{22}O_{11}.H_2O$.

923. Maltose is a sweet sugar, with a density of 1·54: it is very soluble in water, but is almost insoluble in absolute alcohol. It resembles dextrose in many of its properties, and is readily fermented by yeast. Its specific rotatory power is $[\alpha]_D + 137°$ and its osazone fuses at 206°C.

924. **Ignition.**—Maltose loses water when it is heated, and is ultimately decomposed with charring.

925. **Strong H_2SO_4** forms a clear solution with maltose in the cold, but this gradually carbonises and blackens when it is heated

926. **NaOH solution,** when it is boiled with maltose, becomes yellow and finally brown.

927. **Fehling solution** (909) is reduced by maltose.

928. **CuA_2-solution,** mixed with $H\bar{A}$, is not reduced by maltose on boiling (Distinction from glucose.)

929. **Lead acetate,** if it is boiled with maltose solution, and AmOH is then added until a precipitate is produced and the solution is again boiled, yields a precipitate which is finally pink in colour.

930. **Picric acid,** mixed with excess of KOH, yields with maltose the same result as it does with glucose (912).

931. **Dilute Sulphuric acid,** when it is boiled with maltose solution, hydrolyses it, yielding two molecules of dextrose.

932. **Osazone.**—When maltose is heated with $C_6H_5NH.NH_2$ and $H\bar{A}$ (903) a yellow crystalline osazone is produced, which has a melting-point of 206°C.

LACTOSE, OR MILK-SUGAR, $C_{12}H_{22}O_{11}.H_2O$.

933. Lactose is much less soluble in water, and less sweet in taste, than the sugars which have been already described, and is insoluble in absolute alcohol and in ether. Lactose melts at 203·5°C., has a density of 1·52, and is not fermented by pure yeast: its specific rotatory power is $[\alpha]_D + 52{\cdot}5°$, and its osazone melts at 200°C.

934. **Ignition.**—When lactose is heated, water is given off, and charring gradually takes place.

935. **Strong H_2SO_4** produces no change until heat is applied, when blackening is gradually produced, but less readily than with cane-sugar.

936. **NaOH solution** produces a yellow solution when the liquid is boiled, and the colour gradually darkens to brown.

937. **Fehling-solution** (909) and ammoniacal $AgNO_3$ (759, *Note*) are each of them reduced by lactose.

938. **$Cu\bar{A}_2$ and $H\bar{A}$**: no reduction is produced by lactose on boiling, unless the solution is very strong.

939. **Lead acetate,** when it is boiled with lactose solution, and sufficient AmOH is then added to produce a white precipitate, and the liquid is again boiled, produces a yellow precipitate.

940. **Picric acid,** mixed with excess of KOH, behaves with lactose as it does with glucose (912).

941. **Osazone.**—When lactose is heated with $C_6H_5.NH.NH_2$ and $H\bar{A}$, a yellow crystalline osazone is produced, with a melting-point of 200°.

942. SUMMARY OF REACTIONS OF THE SUGARS.

Test.	Glucose.	Sucrose.	Lactose.	Maltose.
Heat in ignition-tube.	Melts, and chars when it is further heated.	Melts, and chars readily.	Chars without previously melting.	Melts, and chars when it is further heated.
Add strong H_2SO_4 and heat.	Chars gradually when it is heated.	Chars in the cold.	Chars gradually when it is heated.	Chars slowly when it is heated.
Heat with NaOH-solution.	Becomes brown.	Does not change.	Becomes brown.	Becomes brown.
Add $Pb\bar{A}_2$-solution and AmOH, and heat gently.	Pink precipitate.	White precipitate.	Yellow precipitate.	Pink precipitate.
Add $Cu\bar{A}_2$-solution and $H\bar{A}$ and heat.	Cu_2O separates on boiling.	No change.	No change.	No change.
Add Fehling-solution and heat.	Cu_2O separates on boiling.	No change.	Cu_2O separates on boiling.	Cu_2O separates on boiling.
Add Phenyl hydrazine and $H\bar{A}$ (903) and heat.	Yellow crystals of glucosazone, M.P. 206°.	No osazone.	Yellow crystals of lactosazone, M.P. 200°.	Yellow crystals of maltosazone, M.P. 206°,
Specific rotatory power.	$[\alpha]_D = +52{\cdot}8°$.	$[\alpha]_D = +66{\cdot}5°$.	$[\alpha]_D = +52{\cdot}5°$.	$[\alpha]_D = +137°$.

CELLULOSE, $(C_6H_{10}O_5)_n$.—Use Cotton-wool.

943. Cellulose is a colourless, insoluble, tasteless substance: it is unaffected by water and by most other solvents, even when it is boiled with them.

944. **Strong H_2SO_4** dissolves cellulose, and when the solution is diluted and boiled, the cellulose is hydrolysed and changed completely into dextrose; after this solution has been neutralised, the dextrose may be detected by means of Fehling-solution (908).

945. **Iodine reaction.**—Cellulose itself gives no reaction with iodine; but after it has been treated with one of the following mixtures (*a*, *b*) iodine produces a blue colour with the product, which is known as "amyloid."

(*a*) A mixture of 90 parts of $ZnCl_2$-solution of 2·0 specific gravity, with 6 parts of KI and 10 parts of water.

(*b*) A mixture of 3 parts of strong H_2SO_4 with 2 parts of glycerol and 1 part of water. This mixture is rubbed with the cellulose in order to effect the necessary change.

946. **Cuprammonium hydroxide,** made by dissolving freshly-precipitated $Cu(OH)_2$ in *strong* ammonia-solution, dissolves cellulose: the cellulose is reprecipitated when an acid is added in excess to the solution.

STARCH.—Use Potato- or Rice-starch in powder, $(C_6H_{10}O_5)_n$.

947. **Starch** is insoluble in cold water, but it yields a transparent liquid when it is *boiled* with water ; this liquid becomes gelatinous as it cools, if much starch is present.

948. **Starch granules** may be identified by their appearance, when they are examined by a quarter-inch object-glass under the microscope. If they are viewed as transparent objects they usually appear round or oval, but they are occasionally irregular in shape, and show dark rings which are more or less concentric. Many kinds of starch-granules show a cross when they are examined by polarised light. These appearances are not visible in starch which has been exposed to heat.

949. **Iodine reaction.**—If starch is boiled with water, and a drop of iodine-solution is added to the *cold* liquid, it will assume an intensely *bluish-black* colour.

This colour disappears when the liquid is heated, but it frequently reappears when the liquid is cooled, if the starch is present in large excess.

The colour is destroyed by the addition in excess of a reducing agent, such as H_2SO_3, $Na_2S_2O_3$, or H_2S : it is therefore prevented from appearing if any one of these substances is present in the starch-solution, until the iodine has been added in excess.

950. **Br and HCl** : if starch is dissolved in a little strong HCl, and Br-water is added, a deep yellow precipitate is formed.

951. **Basic Lead acetate** gives a white precipitate with starch-solution.

952. **Conversion into Dextrin and Glucose.**—When it is boiled with dilute H_2SO_4 for some time, starch is hydrolysed : it is first converted into a mixture of dextrin and glucose, and finally into glucose alone. In the early stages of the process, the dextrin may be detected by giving a red coloration with iodine (954). The glucose may be detected by means of Fehling-solution, after the liquid has been neutralised (908).

DEXTRIN, $(C_6H_{10}O_5)_n$.

953. Dextrin is a white powder, which is soluble in water, but is insoluble in *strong* alcohol. It is therefore precipitated from its aqueous solution by the addition of much alcohol. Its specific rotatory power varies considerably in different specimens.

Dextrin may be made by the hydrolysing starch (952), or by heating starch to 200° for some time. It is a mixture of substances which conform to the general formula $(C_6H_{10}O_5)_n$. It appears to contain the CO group, since it gives a yellow coloration with alkalis and can unite with phenylhydrazine.

954. **Iodine-solution** produces a red colour in the solution of most forms of dextrin.

955. **Fehling-solution** (909), **and CuA_2 in $H\bar{A}$-solution,** are usually *slowly* reduced by dextrin-solution on boiling.

956. **Hydrolysis.**—Dextrin is converted into glucose by being heated for some time with dilute H_2SO_4; when this solution is neutralised and heated with Fehling-solution, red Cu_2O is precipitated (908).

957. **Basic Lead acetate** gives no precipitate with dextrin-solution. (Difference from starch.)

GROUP VII.—GLUCOSIDES.

958. Glucosides are compounds of vegetable origin. When they are hydrolysed, they usually yield glucose, $C_6H_{12}O_6$, and an aromatic compound: thus *salicin* gives glucose and saligenin; *digitalin* gives glucose, digitalose and digitaligenin; and *amygdalin* splits into glucose, hydrocyanic acid and benzaldehyde.

SALICIN, $C_{13}H_{18}O_7$.

959. Salicin occurs in willow-bark; it crystallises in silky needles, and melts at 201°. It has a bitter taste, and is sparingly soluble in cold water and in alcohol, but is more soluble when the liquid is heated. Salicin is insoluble in ether, but is readily soluble in caustic alkalis and in glacial acetic acid.

960. **Ignition:** when salicin is heated in an ignition-tube, it melts, then chars and emits the smell of burnt sugar.

961. **Strong H_2SO_4,** when it is added in small quantity to solid salicin, gives a blood-red coloration.

962. **Ammoniacal $AgNO_3$** (*Note*, 759) and a few drops of KOH-solution, when they are warmed with solution of salicin, give a silver mirror.

963. **Hydrolysis :** when salicin is heated with dilute H_2SO_4, it is hydrolysed and yields glucose and saligenin, or ortho-hydroxy-benzyl alcohol : $C_{13}H_{18}O_7 + H_2O = C_6H_{12}O_6 + C_6H_4CH_2OH.OH$.

A portion of the hydrolysed liquid is rendered alkaline with KOH-solution and is then warmed with Fehling-solution (909); reduction takes place with separation of orange-red cuprous oxide.

A second portion of the hydrolysed liquid is treated with a few drops of $K_2Cr_2O_7$-solution, the suspended saligenin is coloured pink.

Powdered $K_2Cr_2O_7$ and strong H_2SO_4 are added to a third portion of the hydrolysed liquid, the fragrant smell of salicylic aldehyde will be perceived.

If $FeCl_3$-solution is added to a fourth portion of the hydrolysed liquid, a violet coloration will be produced.

964. **Mandelin's reagent** (1046) produces a purple-red coloration.

965. **Froehde's reagent** (1045) gives a violet coloration.

966. **Erdmann's reagent** (1044) gives a bright red coloration with a purple edge.

DIGITALIN, $C_{29}H_{46}O_{12}$.

967. Digitalin occurs in the foxglove. It is a white powder which melts at 217°. Digitalin is slightly soluble in cold water, readily soluble in alcohol and almost insoluble in ether and in chloroform.

By hydrolysis digitalin yields glucose, digitalose and digitaligenin :— $C_{29}H_{46}O_{12} + H_2O = C_6H_{12}O_6 + C_7H_{14}O_5 + C_{16}H_{22}O_2$.

968. **Strong H_2SO_4** gives a yellow coloration, which gradually changes to brown and finally to red.

969. **Strong H_2SO_4 and $K_2Cr_2O_7$:** if digitalin is dissolved in strong H_2SO_4 and a trace of powdered $K_2Cr_2O_7$ is added, a brown coloration is produced which gradually changes to green.

970. **Strong H_2SO_4 and Br-water :** on adding strong H_2SO_4 and subsequently stirring with a glass rod which has been dipped in bromine-water, a reddish-brown coloration is produced.

971. **Ammoniacal $AgNO_3$** (*Note*, 759) and a drop of KOH-solution produce a silver mirror when the liquid is warmed.

972. **Mandelin's reagent** (1046) produces a brown coloration changing to red.

973. **Froehde's reagent** (1045) **and Erdmann's reagent** (1044) ; each of these produces a brown coloration.

AMYGDALIN, $C_{20}H_{27}O_{11}N$.

974. Amygdalin occurs in bitter almonds and in other vegetables ; it has a melting-point of 215°. In contact with water, amygdalin is hydrolysed by an enzyme, "emulsin," which is present in the bitter almond ; the hydrolysis yields glucose, hydrocyanic acid and benzaldehyde :—$C_{20}H_{27}O_{11}N + 2H_2O = 2C_6H_{12}O_6 + HCN + C_6N_5COH$.

975. **Nitrogen :** the presence of nitrogen in amygdalin may be proved by the sodium test (679), or by heating it with soda-lime (678).

976. **Hydrolysis :** when it is heated with dilute H_2SO_4, amygdalin is hydrolysed, yielding glucose, HCN and benzaldehyde.

The presence of *glucose* in the hydrolysed liquid may be shown by Fehling-solution (909) ; HCN may be detected by silver nitrate (691), and benzaldehyde may be found by its smell and by Schiff's reaction (875).

GROUP VIII.—ORGANIC BASES.

977. This Section includes the important bases, aniline, toluidine, pyridine and quinoline ; also the artificial drugs, acetanilide, phenacetin and antipyrine, and the basic substance urea.

ANILINE, $C_6H_5.NH_2$.

978. **Aniline** is a colourless liquid of peculiar smell, but it usually becomes brown by exposure to the air owing to the presence of an impurity. Aniline boils at 184·4°, has a density of 1·0231, and is slightly soluble in water and in alcohol, and readily soluble in ether and in chloroform.

It forms crystalline salts by combination with acids ; and these salts are decomposed, with the liberation of the base, by caustic alkalis, but not by AmOH.

979. **The Salts of Aniline** do not give reaction 980 ; but the base may be liberated from the salts by treating their aqueous solution with KOH, when the aniline will separate in oily drops, and these may be dissolved by shaking the liquid with ether. The

evaporation of this ethereal solution will leave the aniline in the free state, when the test can be applied.

980. **Strong H_2SO_4** dissolves aniline, yielding a colourless solution; if a drop of this solution is added to a little dilute dichromate solution and the solution is stirred, a blue colour will be produced.

981. **Bleaching-powder,** if it is added in small quantity to a very dilute solution of aniline, produces a *mauve* coloration. If this solution is diluted, and a little dilute Am_2S is added to it, a magenta coloration is produced which is not permanent.

982. **Chloroform and alcoholic KOH,** when they are warmed with aniline, evolve the intensely offensive smell of phenyl isocyanide.

983. **Bromine-water** gives a pale pink precipitate of tribromaniline, $C_6H_2Br_3NH_2$.

984. **Diazo reaction.**—To a cold solution of aniline in dilute HCl five drops of KNO_2-solution are added in a test-tube, the mixture being kept cool by holding the tube in cold water: a few drops of β-naphthol dissolved in NaOH are then added: a brilliant scarlet coloration will be produced, which is due to the formation of benzene-azo-naphthol. This reaction is given by all primary aromatic amines.

TOLUIDINE, $CH_3.C_6H_4.NH_2(1:4)$.

985. Paratoluidine crystallises in lustrous scales which have a faint but characteristic smell. Paratoluidine has a melting-point of 45° and a boiling-point of 200°: it is sparingly soluble in water, but more soluble in alcohol.

Toluidine forms crystalline salts with acids, from which the base can be separated by heating them with caustic alkali solutions.

986. **Strong H_2SO_4** dissolves toluidine, and the solution gives a yellow colour when a drop is added to dilute dichromate solution.

987. **HNO_3** gives with toluidine a blue colour, which gradually turns violet, then red, and finally brown.

988. **Bromine,** dissolved in strong HCl, gives with toluidine solution a precipitate of dibromotoluidine.

989. **Bleaching-powder** gives no coloration with toluidine. (Difference from aniline.)

990. **H_2PtCl_6** (*Note*, 420) : yellow crystalline precipitate of $(CH_3.C_6H_4NH_2.HCl)_2PtCl_6$.

991. **Diazo reaction** : if a solution of toluidine in dilute HCl is treated as is described in paragraph 984, it will yield a result similar to that obtained from aniline.

PYRIDINE, C_5H_5N.

992. Pyridine is obtained from bone-oil. It is a colourless liquid, with a strong characteristic smell, which boils at 115·5° and has a density of 0·9893 at 15° C. It is miscible with water in all proportions, giving a liquid with a feebly alkaline reaction, and is soluble in alcohol and in ether.

Pyridine is a strong base, and combines with acids to form salts, which are decomposed by caustic alkalis with liberation of the base.

993. **Strong H_2SO_4** forms a white pyridine salt, which dissolves in excess of the acid to a colourless liquid.

994. **Bromine-water,** when it is added in excess to a solution of pyridine in HCl, gives a yellow precipitate, $C_5H_5NBr_2$.

995. **H_2PtCl_6** gives with a solution of pyridine in HCl an orange-yellow precipitate of the platinichloride, $(C_5H_5N.HCl)_2 PtCl_6$.

996. The reagents which produce precipitates with the alkaloids (1036 *et seq.*) also give precipitates with pyridine.

QUINOLINE, C_9H_7N.

997. Quinoline is obtained from bone-oil and from coal-tar. It is a colourless limpid liquid, with a peculiar aromatic odour, and becomes brown on exposure to the air. It boils at 238°, but volatilises in steam from boiling-water; has a density of 1·0944, is sparingly soluble in water, and more readily soluble in most organic liquids. Quinoline burns with a luminous smoky flame. It is a strong base and yields deliquescent salts by combination with acids.

998. **Strong H_2SO_4** : white crystalline precipitate of the sulphate, soluble in excess of the acid.

999. **H_2PtCl_6** (*Note*, 420) gives with the HCl-solution a yellow precipitate of the platinichloride, $(C_9H_7N.HCl)_2PtCl_6$.

1000. **$K_2Cr_2O_7$** gives with acid solutions of quinoline a fine

yellow precipitate of the dichromate, $(C_9H_7N)_2H_2Cr_2O_7$, which dissolves when the liquid is warmed. (Difference from pyridine.)

1001. The general reagents for the alkaloids (1036–1042) give precipitates with quinoline.

ACETANILIDE, OR ANTIFEBRIN, $C_6H_5.NH.CO.CH_3$.

1002. Acetanilide forms colourless lustrous crystalline plates, which melt at 113° and boil at 283°. It is slightly soluble in cold water, but readily soluble in hot water, in alcohol, in ether and in chloroform.

1003. **H_2SO_4 and $K_2Cr_2O_7$.**—If a little acetanilide is dissolved in strong H_2SO_4 and powdered $K_2Cr_2O_7$ is sprinkled on the surface of the solution, red streaks which quickly turn green will be produced.

1004. **KOH.**—If a little acetanilide is heated with KOH-solution, potassium acetate and aniline are formed :— $C_6H_5.NH.COCH_3 + KOH = C_6H_5NH_2 + CH_3.COOK$.

The aniline thus produced may be recognised by adding a few drops of $CHCl_3$ and warming the liquid, when the badly smelling phenyl isocyanide will be evolved.

1005. **Strong H_2SO_4 and Alcohol,** when they are warmed with acetanilide, produce ethyl acetate, which is recognised by its fragrant smell.

1006. **$HgNO_3$ solution,** if it is poured upon a little acetanilide in sufficient quantity to moisten it, gives on evaporation to dryness a green mass, which becomes deep red when it is moistened with strong H_2SO_4.

1007. **$FeCl_3$ solution,** when it is boiled with acetanilide, produces a turbity but *no red coloration*, although the $FeCl_3$-solution becomes darker in colour. (Distinction from antipyrine and phenacetin.)

1008. **Mandelin's reagent** (1046) produces an orange-red solution, the colour of which changes to red and finally to grey.

PHENACETIN, OR PARA-ACETAMIDO-ETHOXY-BENZENE, $C_6H_5O.C_6H_4.NH.COCH_3$.

1009. Phenacetin forms colourless odourless crystalline scales, which melt at 135°. It is almost insoluble in cold water, fairly soluble in hot water, and readily soluble in ether and in chloroform.

1010. **Ignition :** when it is heated in an ignition-tube phenacetin melts and then sublimes.

1011. **Conversion into salicylic acid.**—When phenacetin is heated with twice its volume of zinc-dust until it is charred, salicylic acid is produced, and may be found by boiling the mass with a little water, filtering and adding $FeCl_3$-solution to the liquid, when a violet coloration will be produced (779).

1012. **Strong H_2SO_4 and alcohol,** when they are warmed with phenacetin, cause the smell of ethyl acetate vapour to be evolved.

1013. **HNO_3** diluted with its own volume of water, when it is warmed with phenacetin, produces an orange-red solution which deposits yellow crystals on cooling. If KOH is then added in excess, a red coloration is produced which becomes deeper in tint when the liquid is boiled.

1014. **H_2SO_4 and $K_2Cr_2O_7$.**—If a few drops of strong H_2SO_4 are added to a little phenacetin in a porcelain dish, and some crushed $K_2Cr_2O_7$ is then sprinkled upon the surface, a green coloration will be produced after a time.

1015. **$FeCl_3$ solution** gives a red coloration when the liquid is warmed.

1016. **Mandelin's reagent** (1046) produces a pale blue coloration.

ANTIPYRIN, OR PHENAZONE, $C_{11}H_{12}N_2O$.

1017. Antipyrin forms colourless odourless crystals, which have a melting-point of 114°, are soluble in water and in alcohol, but are only sparingly soluble in ether: the solution has a bitter taste. Antipyrin is neutral in reaction, but it is a basic substance and forms salts by combining with acids.

1018. **Ignition.**—When antipyrin is heated in an ignition-tube it melts and then chars, and gives a brown liquid sublimate.

1019. **Strong H_2SO_4** dissolves antipyrin, forming a colourless liquid.

1020. **Strong HNO_3,** when it is heated with antipyrin, gives first a yellow and then a deep red coloration.

1021. **$Hg_2(NO_3)_2$** gives a dirty yellowish-green precipitate, and turns deep red and deposits a red precipitate when the liquid is boiled.

1022. **KNO_2 and H_2SO_4.**—If a fragment of KNO_2 and a few drops of dilute H_2SO_4 are added to solution of antipyrin, a bright

green coloration is produced; and if the solution is strong, green crystals are formed.

1023. **H_2SO_4 and $K_2Cr_2O_7$:** this test, applied as directed for phenacetin (1014), gives a green coloration.

1024. **$FeCl_3$ solution**, when it is heated with antipyrin, gives a red coloration.

1025. **Mandelin's reagent** (1046) produces a pale blue colour, which is evanescent.

1026. Most of the general reagents for the alkaloids (1036–1042) produce precipitates with antipyrin.

UREA, OR CARBAMIDE, $CO(NH_2)_2$.

1027. Urea is a colourless crystalline substance: it is very soluble in water and in alcohol, but is almost insoluble in ether. Urea melts and begins to decompose at 132° C., evolving NH_3: its density is 1·323.

1028. **Strong HNO_3**, if it is added to solution of urea, causes the separation of the crystalline nitrate: under the microscope the crystals are seen to be delicate rhomboidal scales.

1029. **Strong $H_2C_2O_4$ solution** produces a white precipitate of urea oxalate; this precipitate consists of needle-shaped crystals.

Since urea oxalate is less soluble in amyl alcohol than in water, the test is made more delicate by dissolving both the urea and the oxalic acid in this solvent instead of dissolving them in water.

1030. **KOH**, when it is heated with urea solution, slowly evolves NH_3 and yields K_2CO_3; the carbonate thus produced may be detected by effervescing on the addition of an acid.

1031. **$Hg_2(NO_3)_2$** yields a white precipitate in urea solution.

1032. **KBrO solution** causes a brisk evolution of CO_2 and N gases from urea and from compounds containing urea.

The KBrO-solution must be freshly prepared, by adding Br-water to KOH-solution until the mixture retains a yellow colour after the liquids have been thoroughly mixed.

A similar reaction takes place when KBrO-solution acts upon a urate or upon an ammonium salt.

1033. **Biuret test.**—If solid urea is heated for a few minutes just above its melting-point, biuret is formed and NH_3 is evolved:—

$$2CO(NH_2)_2 = NH(CO.NH_2)_2 + NH_3.$$

If the residue is then allowed to cool and is extracted with water, and the solution is mixed with several drops of $CuSO_4$-solution and then with NaOH-solution added drop by drop, a *violet* coloration is produced.

1034. **Cyanuric acid :** when urea is more strongly heated (1033), cyanuric acid is formed and remains as a white residue :—$3CO(NH_2)_2 = H_3C_3N_3O_3 + 3NH_3$. If the residue is boiled with water, and this solution is treated with a few drops of AmOH- and $CuSO_4$-solutions successively, a purple precipitate is produced.

GROUP IX.—ALKALOIDS.

1035. The vegetable alkaloids are basic nitrogenous substances, which are capable of forming additive compounds or salts with acids. They usually occur in plants united with organic acids, such as citric, malic, tannic, and meconic ; and they are largely employed in medicine on account of their pronounced physiological action. Most of them are extremely poisonous and possess a bitter taste.

The alkaloids are arranged in the following order. First, quinine, quinidine and cinchonine, which are derived from the cinchona bark ; then follow morphine, apomorphine, codeine, narcotine and papaverine, which are contained in opium prepared from the poppy-fruit. Then come strychnine and brucine, which are contained in the Strychnos Nux Vomica and the St. Ignatius bean ; caffeine or theine contained in coffee and tea ; cocaine in coca-leaves ; veratrine ; atropine, hyoscyamine and hyoscine in Atropa Belladonna ; nicotine in tobacco-leaves, and coniine in Conium Maculatum.

The solutions of the alkaloids are alkaline to test-paper, and the solutions of their salts are either neutral or acid in reaction. The free alkaloids are almost insoluble in water, hence solutions of their salts must be employed for trying the liquid reactions.

GENERAL REAGENTS FOR THE ALKALOIDS.

The following general reagents precipitate most of the alkaloids :—

1036. **Na_2CO_3** precipitates the hydrated alkaloid from strong solutions of its salts.

1037. **Phospho-molybdic acid** (*Note*, page 230) causes a yellow to brown precipitate in the solution of an alkaloid.

Note.—Phosphomolybdic acid is prepared as follows: The solution of ammonium molybdate in nitric acid (1410, 14) is precipitated by the careful addition of sodium phosphate solution (1409, 16). The precipitate is well washed, and is then dissolved in Na_2CO_3-solution. This solution is evaporated to dryness and the residue is ignited. Water is then added and warmed with the residue, which is finally dissolved by adding a considerable excess of HNO_3.

1038. **H_2PtCl_6-solution** (*Note,* 420), acidified with HCl, gives with solution of an alkaloid-salt a yellow crystalline precipitate, similar to that obtained with solution of an ammonium salt.

1039. **Iodine dissolved in KI solution** gives a reddish-brown precipitate in the solution of an alkaloid.

1040. **Ignition.**—When an alkaloid is heated on platinum foil, it burns with a bright smoky flame; and when it is heated with soda-lime, it evolves NH_3.

1041. **Tannic acid** gives a white or brownish precipitate in an alkaloid-solution.

1042. **Picric acid** gives a yellow crystalline precipitate in an alkaloid-solution.

SPECIAL REAGENTS FOR THE ALKALOIDS.

The following special reagents are also used in identifying the alkaloids.

1043. The most convenient way of applying the following and similar reagents for colour tests is as follows:—

Place a trace of the alkaloid or of its salt upon a white tile or in a porcelain dish, and add a drop or two of the reagent by means of a thin glass rod; then stir the liquid with the pointed end of the rod: the colour will be produced and will be easily seen upon the white surface.

1044. **Erdmann's reagent** is prepared by mixing 6 drops of strong HNO_3 with 100 c.c. of water; 12 drops of this solution are then mixed with 24 c.c. of strong H_2SO_4 (1043).

1045. **Froehde's reagent** is made by dissolving 1 gramme of ammonium molybdate in 100 grammes of strong H_2SO_4 (1043).

1046. **Mandelin's reagent** is prepared by dissolving half a gramme of vanadium chloride or oxide in 100 c.c. of strong H_2SO_4 (1043).

1047. **Mayer's reagent** is made by dissolving 13·5 parts of $HgCl_2$ and 50 parts of KI in 940 parts of water.

QUININE; $C_{20}H_{24}N_2O_2.3H_2O$.—Use Quinine sulphate, $C_{20}H_{24}N_2O_2.H_2SO_4.8H_2O$ (1050).

1049. Quinine occurs with quinidine and cinchonine in cinchona bark. It forms a white crystalline mass when it is crystallised from its solution in alcohol; and is slightly soluble in cold water, but more readily soluble in hot water, and in AmOH, alcohol, chloroform, ether, petroleum-spirit and benzene: the aqueous solution is alkaline and is strongly basic. Quinine has a melting-point of 174° C. when it is anhydrous; the crystals melt at 57° and then lose their water of crystallisation.

1050. **Fluorescence.**—When quinine sulphate is being dissolved in water, a few drops of dilute H_2SO_4 should be added; the solution is intensely bitter, and gives a pale blue fluorescence. (Difference from cinchonine.)

1051. **HCl and Ignition.**—When quinine is mixed with HCl and evaporated to dryness, it leave a residue which, when it is ignited, evolves purple vapour similar in appearance to iodine vapour.

1052. **Alkaline hydroxide or carbonate** precipitates hydrated quinine from fairly strong solutions of a quinine-salt; this precipitate disappears when the liquid is shaken with ether.

The corresponding cinchonine precipitate is not dissolved by ether.

1053. **Br-water, or Cl-water,** when it is added in small quantity, does not colour a solution of quinine; but if AmOH is afterwards added, an intense *emerald-green* colour appears, which is due to the formation of thallioquinine.

1054. **Br- or Cl-water and K_4FeCy_6.**—If the addition of Br- or Cl-water to quinine solution is followed by the addition of K_4FeCy_6-solution and one or two drops of KOH-solution, a *deep red* tint is produced. This colour quickly changes to dirty brown: it is destroyed by HĀ, but reappears when AmOH is cautiously added.

1055. **Strong H_2SO_4** dissolves quinine to a colourless solution, which becomes green when a crystal of $K_2Cr_2O_7$ is added.

1056. **$Am_2C_2O_4$** gives a white precipitate, the formation of which is hastened by shaking the liquid. (Difference from quinidine.)

1057. **Mandelin's reagent** (1046) gives no change, but on the further addition of a drop of HNO_3 a violet coloration is produced.

QUINIDINE, $2C_{20}H_{24}N_2O_2.5H_2O$.

1058. Quinidine, when it is crystallised from alcohol, forms white efflorescent needles which contain two molecules of water. Anhydrous quinidine melts at 171·5°: it is soluble in water, in ether and in alcohol.

1059. **Strong H_2SO_4,** when it is poured upon a particle of quinidine, forms a colourless solution, which turns green when a crystal of $K_2Cr_2O_7$ is added.

1060. **$Am_2C_2O_4$** gives no precipitate with quinidine. (Difference from quinine.)

1061. **Br–water** (1053), **HCl and ignition** (1051), **and Mandelin's reagent** (1057), give reactions with quinidine similar to those given with quinine.

CINCHONINE, $C_{19}H_{23}N_2O$.

1062. Cinchonine crystallises in white lustrous prisms, and melts at 255° to a colourless liquid, which partly sublimes when it is further heated. Cinchonine is sparingly soluble in water, but more soluble in alcohol, in ether and in chloroform. Solutions of cinchonine have an alkaline reaction and a bitter taste.

1063. **Cl–water, or Br–water,** when it is added to a cinchonine-solution, produces no change; but on the further addition of AmOH, a yellowish-white precipitate appears. (Difference from quinine.)

1064. **K_4FeCy_6** gives a yellow precipitate of cinchonine ferrocyanide, which is readily soluble in excess. The precipitate is soluble in hot water, and crystallises in golden-yellow crystals as the solution cools. This is a characteristic reaction.

1065. **Strong H_2SO_4 and $K_2Cr_2O_7$** (1055), **HCl and ignition** (1051), **and Mandelin's reagent** (1057) give with cinchonine changes similar to those given with quinine.

MORPHINE, $C_{17}H_{19}NO_3$.—Use Morphine hydrochlorate, $C_{17}H_{19}NO_3.HCl.3H_2O$.

1066. Morphine meconate is present with apomorphine, codeine, narcotine and papaverine in poppy-fruit, and in opium prepared

from the fruit. Morphine crystallises in colourless prisms, which contain one molecule of combined water: these become anhydrous at 120°, and melt at 230°C.

Morphine is almost insoluble in water, ether, and alcohol; it is slightly soluble in hot water, but readily soluble in chloroform, benzene, and amyl alcohol, and the solution has an alkaline reaction. The salts of morphine are readily soluble in water and in alcohol.

1067. KOH or AmOH yields a white precipitate of the base, which is soluble in excess of KOH, but is only sparingly soluble in excess of AmOH.

1068. HNO_3.—The strong acid produces a *yellowish red* colour, which does not change to *violet* on the addition of $SnCl_2$. (Difference from brucine.)

1069. $FeCl_3$ solution: if the neutral solution is added drop by drop to neutral morphine solution, it produces a *dark blue* colour: this colour disappears when an acid is added.

1070. Iodic acid, when it is added to morphine or to its salts, yields free iodine. The separation of iodine is shown by the liquid becoming brown; but the iodine is more certainly and readily detected by adding starch-solution, or by shaking the liquid with CS_2 (555, 2, 3). The brown coloration of the solution becomes more intense on the addition of AmOH.

This test is rendered very delicate and characteristic by moistening the solid substance with a solution of one part of iodic acid in fifteen of water, and then adding a solution of one part of starch in four hundred of water; when very dilute AmOH is poured upon the blue solution thus obtained, a coloured ring is seen at the surface of contact of the two liquids; the ring is *blue* below and *brown* above.

This reaction serves to distinguish morphine from other organic substances which contain nitrogen.

1071. H_2SO_4 gives no colour when it is added to a solution containing morphine; but when a crystal of $K_2Cr_2O_7$ is dropped into the acid liquid contained in a white porcelain dish, and the crystal is slowly moved about with a glass rod, an *intense green* colour appears. Quinine gives a similar reaction.

1072. H_2SO_4 and $K_2Cr_2O_7$.—If solid morphine, or any of its compounds, is dissolved by heating it with a few drops of strong H_2SO_4, and a minute quantity of HNO_3 is added to the cold solution, a deep red colour is produced. This colour turns to a mahogany tint when a fragment of $K_2Cr_2O_7$ is dropped into the liquid.

1073. **Froehde's reagent** (1045) gives a purple coloration, which becomes green and finally yellowish-brown.

1074. **Mandelin's reagent** (1046) produces a dull purple coloration which changes to grey.

APOMORPHINE, $C_{17}H_{17}NO_2$.

1075. Apomorphine is a white amorphous substance, melting at 295°. It is slightly soluble in water, but readily soluble in alcohol, ether, benzene and chloroform. Solutions of the free base rapidly become green in colour and finally brown.

1076. **HNO_3** produces a purple-red coloration, which rapidly changes to brown.

1077. **$FeCl_3$ solution** gives a purple-red coloration, which becomes dark brown when the liquid is heated.

1078. **Strong H_2SO_4 and $K_2Cr_2O_7$**: when a drop of strong H_2SO_4 is poured upon a trace of apomorphine, and particles of $K_2Cr_2O_7$ are then sprinkled on the surface of the acid, an olive-green coloration is produced, which changes to brown.

1079. **Mandelin's reagent** (1046) produces a bluish coloration.

1080. **Froehde's reagent** (1045) gives a deep green coloration, which gradually becomes blue.

CODEINE (Methyl-morphine), $C_{17}H_{17}NO(OCH_3)OH$.

1081. Codeine crystallises from water in prisms, which contain one molecule of water. It is fairly soluble in hot water; readily soluble in alcohol, ether, chloroform, benzene and amyl alcohol; but insoluble in ligroin. Its salts are soluble in water. Codeine is a strong base, with a melting point of 155° C., and an alkaline reaction to test-papers.

1082. **Strong H_2SO_4** dissolves codeine to a colourless solution, which becomes blue when it is warmed, and reacts as follows:—

(1) $FeCl_3$ produces in the *cold* H_2SO_4-solution a blue coloration.

(2) If cane-sugar is ground up with the H_2SO_4-solution in a mortar, a purple-red coloration appears after a time.

(3) When a drop of strong HNO_3 is added to the H_2SO_4-solution, a deep red coloration is produced.

1083. **Formalin**: when a little codeine is moistened with

ormalin, and a few drops of strong H_2SO_4 are added, a violet colour produced.

1084. **Mandelin's reagent** (1046) gives a greenish-blue coloraon.

1085. **Froehde's reagent** (1045) gives a green coloration, hich changes to blue and finally to yellow.

NARCOTINE, $C_{22}H_{23}NO_7$.—Use Narcotine, or its sulphate.

1086. Narcotine forms lustrous prisms or needles, which have melting-point of 176°. It is almost insoluble in water, slightly oluble in alcohol and in ether, but readily soluble in chloroform. Narcotine is a feeble base, and its salts have an acid reaction, since hey are partially hydrolysed in an aqueous solution.

1087. **H_2SO_4:** the strong acid gives a *bluish-violet* coloration, which changes to orange; with some specimens a yellow solution s produced at once.

When this liquid is gradually warmed, it becomes first *orange-ed* and then *bluish-violet*, or *purple* stripes proceed from the edge f the liquid surface: when the liquid is cooled, the colour changes o *cherry-red*. If the heating is pushed to the initial evaporation f the acid, an intense *reddish-violet* colour appears.

1088. **H_2SO_4 and $K_2Cr_2O_7$.**—If narcotine is subjected to the eaction which has been already described for morphine (1072), n intense red coloration is produced.

1089. **HNO_3:** strong nitric acid produces a yellow coloration in he cold liquid: this changes to red when the liquid is heated, but ades to yellow again as it cools.

1090. **Erdmann's reagent** (1044) produces an orange-yellow olution, which turns pink and then rapidly becomes yellow again.

1091. **Mandelin's reagent** (1046) gives an orange coloration, which rapidly becomes pink.

1092. **Froehde's reagent** (1045) gives a deep green coloration.

PAPAVERINE, $C_{20}H_{21}NO_4$.

1093. Papaverine is a white crystalline substance which melts t 14[illegible]. It is insoluble in water, sparingly soluble in ether, n b[illegible]e and in cold alcohol, but readily soluble in chloroform nd [illegible]t alcohol. Its salts are soluble in water.

1094. **Strong H_2SO_4** dissolves papaverine giving a colourless solution, which becomes violet when it is warmed.

1095. **$K_2Cr_2O_7$**, when it is added to the acid solution, yields an orange-yellow precipitate of the bichromate.

1096. **Cl-water and AmOH,** if they are added successively, yield a reddish-brown colour, which changes to very dark brown.

1097. **Iodine-solutions** gives a dark-red coloration.

1098. **Froehde's reagent** (1045) gives a green coloration which changes to blue and finally to cherry-red.

1099. **Mayer's reagent** (1047) gives a white or yellowish-white precipitate.

STRYCHNINE, $C_{21}H_{22}N_2O_2$.

Use strychnine, or its sulphate, dissolved in water to which a drop of dilute H_2SO_4 has been added.

1100. Strychnine is prepared from Strychnos nux vomica, and from the St. Ignatius bean. It crystallises in colourless prisms which melt at 265°. Strychnine is almost insoluble in water, absolute alcohol, ether and benzene, more soluble in dilute alcohol, and readily soluble in alcohol.

The salts of strychnine are soluble in water and in alcohol. All strychnine solutions possess an intensely bitter taste : one part of strychnine in 700,000 parts of solvent can be recognised by its taste. Both strychnine and its salts are *virulent poisons.*

1101. **H_2SO_4 and $K_2Cr_2O_7$.**—Strychnine dissolves in strong H_2SO_4 to a colourless liquid. When a fragment of $K_2Cr_2O_7$ is added to this solution in a porcelain dish, and is slowly moved about by pushing it with a glass rod, a *bluish-violet* coloration is produced which gradually changes to red or yellow.

The presence of morphine, or of a metallic chloride or nitrate, interferes with this reaction. If any of these substances are present, the strychnine may be precipitated by the addition of solution of K_3FeCy_6, or of K_2CrO_4; the precipitate is filtered off and slightly washed on the filter, and is then stirred with strong H_2SO_4.

1102. **HNO_3**: cold strong nitric acid dissolves strychnine without becoming coloured, but the solution acquires a yellow tint when it is heated.

1103. **Mandelin's reagent** (1046) gives a blue colour, which changes to violet. The addition of AmOH changes the colour to rose-red. (Difference from other alkaloids.)

BRUCINE, $C_{23}H_{26}N_2O_4.4H_2O$.

Use Brucine or its sulphate, dissolved in water to which a drop of H_2SO_4 has been added.

1104. Brucine is derived from the same sources as strychnine. It forms colourless prisms or needles: these lose $4H_2O$ at 100°, and the anhydrous base melts at 178°. Brucine is slightly soluble in water and in ether, but readily soluble in alcohol, in amyl alcohol and in chloroform: its salts are readily soluble in water.

1105. HNO_3: the strong acid yields an *intensely red* coloration, which gradually changes to yellowish-red and yellow when the liquid is evaporated. After all the HNO_3 has been driven off by evaporation, the addition of $SnCl_2$ to the hot solution produces an intense *violet* colour. (Difference from morphine.)

1106. H_2SO_4: the strong acid produces a *rose-coloured* solution, which changes to *yellow*.

1107. H_2SO_4 and $K_2Cr_2O_7$: if the reaction which has already been described for morphine (1072), is carried out with brucine, the liquid becomes red but quickly changes to yellow.

1108. Erdmann's reagent (1044) produces a yellow coloration, which changes to intense red.

1109. Froehde's reagent (1045) gives a pale red coloration, which changes to deep reddish-brown.

1110. Mandelin's reagent (1046) gives a rose coloration, which rapidly changes to orange.

CAFFEINE, OR THEINE, $C_8H_{10}N_4O_2.H_2O$.

111. Caffeine is present in coffee and in tea, and is a colourless substance forming needle-like crystals, which become anhydrous at 100° C., then melt at 230·5° C., and sublime unchanged at 237° C. Caffeine is slightly soluble in cold water, readily soluble in hot water, and fairly soluble in alcohol, in ether and in chloroform. It is a weak base, its salts being hydrolysed by water.

1112. Formation of Murexide.—If strong HNO_3 is mixed with even a trace of caffeine and is then evaporated, a yellow residue remains, which assumes an intense purple colour when AmOH is poured upon it.

1113. Cl- or Br-water, if it is added to caffeine and the mixture is evaporated, leaves a brown residue: this residue dissolves in AmOH, yielding a violet-red solution.

1114. Strong H_2SO_4 dissolves caffeine: when powdered $K_2Cr_2O_7$ is added to the colourless solution, a green coloration gradually appears.

1115. KOH: when caffeine is boiled with KOH-solution, the characteristic fish-like smell of trimethylamine is perceived.

1116. Mayer's reagent (1047) gives no precipitate with caffeine. (Distinction from other alkaloids.)

COCAINE, or Methyl-benzoyl-ecgonine, $C_{17}H_{21}NO_4$.
Use Cocaine hydrochloride.

1117. Cocaine is the active alkaloid which is present in coca leaves. It forms colourless prisms, which melt at 98°, and are sparingly soluble in water, but readily soluble in organic liquids. Cocaine is a strong base and its salts are soluble in water.

1118. **Strong H_2SO_4** does not colour cocaine, but the subsequent addition of a fragment of $K_2Cr_2O_7$ produces a brown coloration.

1119. **Strong $KMnO_4$ solution** gives a purple precipitate of cocaine permanganate.

1120. **K_2CrO_4 solution,** if it is added to cocaine-solution after a few drops of HCl, produces a yellow precipitate. This is a characteristic reaction.

1121. **Strong H_2SO_4 and alcohol,** when they are added to cocaine, cause a fragrant smell of ethyl benzoate to be emitted when the liquid is warmed.

1122. When cocaine is heated with an acid, it undergoes hydrolysis and yields ecgonine, methyl alcohol and benzoic acid.

VERATRINE OR CERAPINE, $C_{32}H_{42}NO_9$.

1123. Veratrine is an amorphous white powder, which melts at 205°, and is insoluble in water, but soluble in organic liquids. It possesses no smell, but it causes violent sneezing when it is inhaled even in minute quantity.

1124. **Strong H_2SO_4** produces a yellow coloration: this colour changes to intense red when the liquid is heated.

1125. **Sugar and H_2SO_4:** when veratrine is mixed with four times its volume of cane-sugar, and the mixture is moistened with strong H_2SO_4, the coloration is first yellow, then green and finally indigo-blue.

1126. **Strong HCl** gives no coloration to veratrine, but when the liquid is boiled an intense red coloration is produced.

1127. **Froehde's reagent** (1045) produces a red coloration, which gradually becomes green.

ATROPINE, $C_{17}H_{23}NO_3$.

1128. Atropine, together with hyoscyamine and hyoscine, is present in the deadly nightshade, Atropa belladonna. It is white

and crystalline, melts at 115°, and is almost insoluble in water, but fairly soluble in ether and benzene, and readily soluble in alcohol and chloroform. It forms salts with acids, is very poisonous, and is employed in ophthalmic surgery.

1129. **Strong H_2SO_4** dissolves atropine; the colourless solution becomes brown when it is warmed, and emits a fragrant smell.

1130. **Fuming HNO_3,** if it is added to atropine and then evaporated to dryness over the water-bath, leaves a residue which, when it is treated with a drop of alcoholic potash, gives a violet coloration changing to red.

1131. **$Ba(OH)_2$ solution,** if it is added to atropine, and the liquid is then evaporated to dryness, leaves a residue which, when it is heated strongly, emits a smell of hawthorn-blossom.

1132. **$HgCl_2$ solution,** when it is added to an alcoholic solution of atropine, gives a yellow precipitate.

1133. **Gold chloride:** if atropine is dissolved in dilute HCl, and a 5 per cent. solution of gold chloride is added, a precipitate is formed of the aurichloride, $C_{17}H_{23}NO_3HCl.AuCl_3$: this precipitate has a melting-point of 136°, and fuses when it is heated with water, forming oily drops. (Distinction from hyoscyamine and hyoscine.)

1134. **Picric acid** gives a yellow precipitate, which has a melting-point of 175–176° C.

HYOSCYAMINE, $C_{17}H_{23}NO_3$.

1135. Hyoscyamine is isomeric with atropine, and is converted into atropine by heat. It is sparingly soluble in water, but is readily soluble in organic liquids. It has a melting-point of 108°.

1136. **Strong HNO_3** gives a red coloration.

1137. **Gold chloride** solution (1133) gives a yellow precipitate, which has a melting-point of 165°, and which does not melt when it is heated under water. (Difference from atropine.)

1138. **Picric acid** forms a picrate, melting at 161°–163°C.

HYOSCINE, or Scopalamine, $C_{17}H_{21}NO_4$.

1139. This alkaloid, formerly thought to be isomeric with atropine, is soluble in water and most organic liquids, and melts at 59°C.

1140. Hyoscine is distinguished from atropine and hyoscyamine by the high melting-point (198°–200°C.) of its aurichloride (1137), which does not fuse under hot water. The picrate has a melting-point of 180°–181°C.

NICOTINE, $C_{10}H_{14}N_2$.

Use nicotine dissolved in five times its volume of water.

1141. Nicotine is present in combination with malic and citric acids in tobacco-leaves. It is a colourless oily liquid, which boils at 247°, undergoing meanwhile partial decomposition. It rapidly turns brown by exposure to the air, and its tobacco-like odour becomes intensified. It distils unchanged in a current of steam, and is readily soluble in water, ether and alcohol. It forms two series of salts.

1142. Strong H_2SO_4 is not coloured by nicotine in the cold, but it becomes brown when it is heated with nicotine.

1143. Formaldehyde: if a little nicotine is treated with one drop of formaldehyde and then with two drops of nitric acid, a pink coloration is produced. (Distinction from coniine.)

1144. Mayer's reagent (1047) gives a reddish precipitate of $C_{10}H_{14}N_2.HgI_4$ even with extremely dilute solutions of nicotine: this is a very characteristic reaction.

CONIINE, or Propyl piperidine, $C_8H_{17}N$.

1145. Coniine is obtained from the spotted hemlock, *Conium maculatum.* It is a colourless liquid with a stupefying odour, and is very poisonous. Coniine boils at 166°, volatilises with steam, and is soluble in water and in organic solvents. It is a strong base and forms neutral salts with acids.

1146. Strong H_2SO_4 has no action on coniine when cold, but blackens when it is heated with coniine.

1147. Strong H_2SO_4 and $K_2Cr_2O_7$ quickly produce a green colour.

1148. Alcohol, CS_2 and $CuSO_4$. Add two drops of alcohol, one drop of coniine-solution, then two drops of CS_2, and allow the mixture to stand: then add one drop of dilute $CuSO_4$-solution: a brown colour will be produced. (Difference from nicotine.)

PART III

SYSTEMATIC ANALYTICAL COURSE AND TABLES

1200. **Preliminary Remarks.**—The analysis of a substance may be undertaken to prove its complete composition and to prove that no other constituents are present, or it may be desired to ascertain only whether any particular substances are present in it.

The procedure to be adopted in the examination and analysis of a substance depends upon the nature of the substance. For this purpose it is to be generally noted whether the substance is a gas (*a*), a liquid (*b*), a non-metallic solid (*c*), or a metal or alloy (*d*).

(*a*) The method of examining gaseous substances is indicated in par. 1201 by giving a statement of the distinguishing properties of some of the more commonly occurring gases; the scheme for the analysis of a gaseous mixture involves a consideration of the properties of the gases which the mixture may contain.

(*b*) The examination of a liquid is described in pars. 1213 *et seq.*

(*c*) The examination of a non-metallic solid will be found in pars. 1215 *et seq.*

(*d*) The examination of a metallic substance is given in pars. 1299–1305.

Special Tables follow, which provide for the analysis of insoluble substances (1306–1311), of silicates (1312–1315), of substances containing cyanogen (1316–1322), of the rarer inorganic elements (1323, 1324), and of organic compounds (1330–1346).

1140. Hyoscine is distinguished from atropine and hyoscyamine by the high melting-point (198°–200°C.) of its aurichloride (1137), which does not fuse under hot water. The picrate has a melting-point of 180°–181°C.

NICOTINE, $C_{10}H_{14}N_2$.

Use nicotine dissolved in five times its volume of water.

1141. Nicotine is present in combination with malic and citric acids in tobacco-leaves. It is a colourless oily liquid, which boils at 247°, undergoing meanwhile partial decomposition. It rapidly turns brown by exposure to the air, and its tobacco-like odour becomes intensified. It distils unchanged in a current of steam, and is readily soluble in water, ether and alcohol. It forms two series of salts.

1142. **Strong H_2SO_4** is not coloured by nicotine in the cold, but it becomes brown when it is heated with nicotine.

1143. **Formaldehyde:** if a little nicotine is treated with one drop of formaldehyde and then with two drops of nitric acid, a pink coloration is produced. (Distinction from coniine.)

1144. **Mayer's reagent** (1047) gives a reddish precipitate of $C_{10}H_{14}N_2.HgI_4$ even with extremely dilute solutions of nicotine: this is a very characteristic reaction.

CONIINE, or Propyl piperidine, $C_8H_{17}N$.

1145. Coniine is obtained from the spotted hemlock, *Conium maculatum*. It is a colourless liquid with a stupefying odour, and is very poisonous. Coniine boils at 166°, volatilises with steam, and is soluble in water and in organic solvents. It is a strong base and forms neutral salts with acids.

1146. **Strong H_2SO_4** has no action on coniine when cold, but blackens when it is heated with coniine.

1147. **Strong H_2SO_4 and $K_2Cr_2O_7$** quickly produce a green colour.

1148. **Alcohol, CS_2 and $CuSO_4$.** Add two drops of alcohol, one drop of coniine-solution, then two drops of CS_2, and allow the mixture to stand: then add one drop of dilute $CuSO_4$-solution: a brown colour will be produced. (Difference from nicotine.)

PART III

SYSTEMATIC ANALYTICAL COURSE AND TABLES

1200. **Preliminary Remarks.**—The analysis of a substance may be undertaken to prove its complete composition and to prove that no other constituents are present, or it may be desired to ascertain only whether any particular substances are present in it.

The procedure to be adopted in the examination and analysis of a substance depends upon the nature of the substance. For this purpose it is to be generally noted whether the substance is a gas (*a*), a liquid (*b*), a non-metallic solid (*c*), or a metal or alloy (*d*).

(*a*) The method of examining gaseous substances is indicated in par. 1201 by giving a statement of the distinguishing properties of some of the more commonly occurring gases; the scheme for the analysis of a gaseous mixture involves a consideration of the properties of the gases which the mixture may contain.

(*b*) The examination of a liquid is described in pars. 1213 *et seq.*

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Special Tables follow, which provide for the analysis of insoluble substances (1306–1311), of silicates (1312–1315), of substances containing cyanogen (1316–1322), of the rarer inorganic elements (1323, 1324), and of organic compounds (1330–1346).

SECTION VI

DETECTION OF GASES

1201. Certain Distinctive Properties of each Gas render its detection possible, when it is alone or when it is mingled with other gases. These distinctive properties of each of the more commonly occurring gases are stated below.

The student may proceed to apply these properties as tests for the detection of gases occurring singly and in a state of mixture. The following facts and suggestions will be of use, when such an examination is to be made. All gases are colourless unless it is otherwise stated.

When a mixture of gases is being examined, it should be remembered that those which act chemically upon one another cannot be simultaneously present. Such mutually exclusive pairs of gases are :—O and NO ; HCl and NH_3 ; SO_2 and H_2S ; Cl and H_2S ; NH_3 and SO_2 ; H and Cl in daylight.

In testing for the constituents of a gaseous mixture, the colour, the odour if not dangerous, and the combustibility should be noted. An examination of the properties stated below shows that a brief exposure of a part of the mixture to air would detect NO ; shaking another portion with water, followed by the examination of separate portions of this solution, would detect HCl, NH_3, SO_2, H_2S, Cl, CO_2 ; the application of a flame or spark to another portion of the mixture would detect O, H, N, H_2S, CO, CH_4, C_2H_4 and C_2H_2 ; and an examination of the products of combustion of a combustible gas will often identify the gas. Special confirmatory tests should be applied, when possible, to support the conclusions drawn from the above general tests.

Some gases are difficult to detect when certain other gases are mingled with them in large proportion. Advantage may frequently be taken of their solubility in water or in solution of caustic alkali to remove these interfering gases and to facilitate the detection of insoluble gases.

Acetylene, C_2H_2, has an offensive smell as it is ordinarily prepared in an impure condition from calcium carbide : it burns with a smoky flame producing water and carbon dioxide (474), and gives with ammoniacal cuprous chloride solution a red precipitate : it is absorbed by Br-water.

Ammonia, NH_3, possesses a pungent smell, gives dense white fumes with hydrogen chloride gas (426), dissolves in water, and the aqueous solution turns red litmus blue and turmeric brown : it is absorbed by dilute H_2SO_4.

Carbon dioxide, CO_2, extinguishes flame, is incombustible, makes lime-water milky (474), dissolves slightly in water giving a solution which renders lime-water milky.

Carbon monoxide, CO, is not soluble in water, burns with a blue flame forming no water, and after the combustion carbon dioxide is found by shaking the product with lime-water (474) : it is absorbed by a solution of Cu_2Cl_2 in HCl or in AmOH-solution.

Carbonyl chloride, $COCl_2$, is a colourless gas with an unpleasant and pungent smell : it is decomposed by contact with water into CO_2 (474) and HCl (543), and yields urea (1027) when it is heated with NH_3.

Carbonyl sulphide, COS, is a colourless gas, with a resinous smell faintly resembling that of H_2S : it burns with a blue flame which deposits S on a cold surface, and forms CO_2 and SO_2. This gas is slightly soluble

in water, undergoing gradual change into CO_2 and H_2S: it is quickly absorbed by caustic alkali solution forming carbonate and sulphide.

Chlorine possesses a peculiar smell and causes coughing, a taper burns in the gas with a red and smoky flame: chlorine dissolves slightly in water, and the aqueous solution bleaches litmus (499, 544); both the gas and its solution turn paper which has been soaked in solution of starch and potassium iodide blue (555).

Cyanogen, C_2N_2, is an intensely poisonous gas with a disagreeable smell; it burns with a flame of peach-blossom colour, which forms no water: it is somewhat soluble in water, and brownish flocks separate from the solution on standing: it dissolves in alkaline hydroxide solution with production of cyanide and cyanate, which may be identified by tests (689, 697): if H_2S is passed into an aqueous solution of cyanogen it gives a red crystalline precipitate.

Ethylene, C_2H_4, has a very faint smell, burns with a very luminous and somewhat smoky flame producing water and carbon dioxide (474), decolorises bromine-water, and is slightly soluble in water, but is not absorbed by Cu_2Cl_2-solution.

Hydrogen burns with a non-luminous flame, which deposits moisture on a cold surface, forming water but no carbon dioxide (474); it is not soluble in water.

Hydrogen chloride, HCl, fumes in the air, and gives dense white fumes with ammonia gas; it dissolves in water and the aqueous solution reddens blue litmus, and gives a white curdy precipitate when it is mixed with silver nitrate solution (543). HCl is found in presence of Cl by par. 545.

Hydrogen sulphide, H_2S, possesses a foul smell; it burns with a blue flame which deposits S on a cool surface, and yields water and sulphur dioxide (489); and it dissolves in water, the aqueous solution blackening lead acetate solution (480).

Methane, CH_4, is free from smell, burns with a slightly luminous flame producing water and carbon dioxide (474), does not decolorise bromine-water, and is not soluble in water.

Nitrogen is incombustible, extinguishes a flame, and gives negative results with all the tests which are mentioned for other gases.

Nitrogen monoxide, N_2O, is colourless, is unchanged by contact with air, has a sweetish taste, does not colour nitric oxide, kindles a glowing splinter into flame and produces a pale yellowish-green halo around the flame.

Nitric oxide, NO, is colourless, but becomes reddish-brown when it is mixed with air or with oxygen.

Oxygen kindles a glowing splinter into flame, and gives a reddish-brown gas with nitric oxide; it is not appreciably soluble in water, but is absorbed by alkaline solution of pyrogallol.

Ozone, O_3, has a smell resembling chlorine diluted with air. It is a powerful oxidiser, bleaching moist litmus and indigo, and liberating I from KI-solution. Ozone may be distinguished from H_2O_2 and nitrogen oxides by passing unchanged through $KMnO_4$-solution, and by giving a violet coloration to test-paper dipped in alcoholic solution of tetra-methyl-diamino-diphenyl-methane (631, 632).

Sulphur dioxide, SO_2, possesses a pungent smell; it dissolves in water and the aqueous solution turns blue litmus red, and changes the red colour of a drop of potassium dichromate solution to green (489).

SECTION VII

ANALYSIS OF LIQUIDS AND SOLIDS

Before commencing work by the General Course (1211 *et seq.*) the following remarks (1202–1210) should be read.

1202. **General Remarks.**—It is usually possible to determine by the qualitative analysis of a substance not only the constituents which it contains, but also roughly the relative proportions in which some of these constituents are present. Many of these constituents are precipitated in the course of the analysis, and the volume of each of the precipitates will give an indication of the amount of the constituent which it represents.

This rough estimate is made more exact if a known weight of the substance, say one gramme, is used for the analysis, and the volume of any precipitate obtained from its solution is compared with the volume of the similar precipitate which is obtained from a known weight of the constituent element to be estimated.

In some complex mixtures it is not possible to determine in this way the relative amounts of the different components, but a general idea may often be gained by observing the colour, the solubility and other properties of the complex mixture.

The usual procedure in examining a liquid or solid substance may be divided into three parts :—

1. The Preliminary Examinations for Metals and Acid-radicles.
2. The Wet Examination for Metals.
3. The Wet Examination for Acid-radicles.

The detailed directions for these Examinations are tabulated as far as is possible, the requisite precautions to be observed being also stated.

Until the student is familiar with the general procedure it will be found advisable to read completely through each part of the text before commencing the Examination.

PRELIMINARY EXAMINATION OF A COMPLEX SUBSTANCE.

1203. Before the student proceeds to apply the whole of the Systematic Course to the analysis of substances of complex composition, he will do well to examine a few substances for Metals and Acid-radicles by the Preliminary tests only, which are given in paragraphs 1213–1228. For a detailed account of any test in these Tables the student must refer back to the description of that test which is given in Part II.

A little study of the Tables 1218–1228 will show that they contain certain principal tests marked thus—"Exp. I." These stand in the first column. In the second column are placed in succession the results which may be noticed on trying these experiments; a glance through these will forewarn the student of what has to be looked for.

The main classification of the observations which may be made is indicated by black-type letters; the subsidiary divisions are marked by small numbers and italics; and the individual results are simply placed in succession in a vertical column.

Occasionally an observation is made which it is advisable to confirm by an additional experiment. This Confirmatory-test is entered in the first column just below the original observation, and is marked *Confirmatory* in order to distinguish it from the main experiment; its results are placed beside it in the second column.

The student should understand that he may obtain any of the results which are entered in the second column.

FULL EXAMINATION OF SUBSTANCES IN SOLUTION.

1204. After the student has become familiar with the Preliminary Examination of solid and liquid substances, he should fully analyse some easy substances which contain only a few metals and acid-radicles. A beginning is made at paragraph 1215, and after the Preliminary Examination has been finished, the substance is dissolved, and a Systematic Examination of its solution is made.

The following paragraphs (1205–1210) give a general explanation of the method of making and examining the solution for metals, and also state some points which require attention during the procedure which is stated in the General Table (1235).

1205. **It is necessary first to separate the Metals into Groups** from the solution, by adding the Group-Reagents (82) in such order that each reagent precipitates the metals of one Group only, and leaves in solution the metals of all other Groups which may be present.

This is effected by adding the Group-Reagents to the solution of the substance in the order which is directed in the General Table (1235): the metal-groups will thus be precipitated in succession, the metals of the Potassium or Fifth Group alone being left in solution.

The different Metal-groups, in the order of their analytical separation from one another, are those into which the metals have already been divided for the description of their reactions in Part II.

Each of these Groups has been designated by its Group-number, or by its Group-precipitant, or by some well-known member of

the Group. As has been stated (82), the designation by number is the least safe, since some analysts number the groups differently.

The Analytical Groups are as follows and, omitting the rarer metals, they contain the metals indicated :—

Group I., or HCl-group, or Silver-group (Ag, Pb, Hg).
*Group II.*A.–B., or H_2S-group :—
A. Copper-group (Cu, Hg˙, Pb, Bi, Cd).
B. Arsenic-group (As, Sb, Sn).
*Group III.*A., or AmOH-group, or Iron-group (Fe, Al, Cr).
*Group III.*B., or Am_2S-group, or Zinc-group (Zn, Mn, Ni, Co).
Group IV., or Am_2CO_3-group, or Barium-group (Ba, Sr, Ca).
Group V., or Potassium-group (K, Na, Li, NH_4, Mg).

Taking these Groups as they stand in the General Table (1235) :—

The first Reagent added is HCl, which precipitates only the metals of Group I., and leaves the metals of Groups II., III., IV. and V. in solution. Hence if a precipitate is obtained when HCl is added in excess, it is filtered off; any member or members of Group I. will then be present upon the filter, while the members of all other Groups will remain in the filtrate.

When H_2S is passed into the Filtrate (*Note*) metals of Group II. alone will be precipitated and may be filtered off.

AmCl and excess of AmOH are added to the Filtrate, (*Note*) after the H_2S has been removed from it and Fe has been converted into ferric salt by boiling it with HNO_3. The AmOH will precipitate any members of Group III.A., which may be filtered off, while Group III.B. and Mg will remain dissolved by the AmCl, and Groups IV. and V. will also remain in solution.

The addition of Am_2S to the Filtrate (*Note*) will then precipitate Group III.B. as sulphides, which are removed by filtration.

Group IV. is then precipitated from the Filtrate (*Note*) by the last Group-Reagent, Am_2CO_3, and any precipitate is filtered off.

The Filtrate, or *Solution* if Am_2CO_3 has caused no precipitate, *is examined for Group V.*, the members of which are not precipitated by any Group-Reagent, and will therefore now remain in solution if they were present in the original liquid.

Note.—Or into the solution, supposing no precipitate to have been obtained, and filtration therefore to have been unnecessary.

1206. Addition of Reagents in Excess.—Each Metal-Group must be *completely* precipitated before the next Group-Reagent is added. If any precipitate has been formed by a Group-Reagent, it is accordingly necessary to add that reagent *in excess* before proceeding to add the next one. Unless the presence of each reagent

in excess is proved before proceeding, much confusion may be caused.

The general method for ascertaining that a Group-Reagent is present in excess consists in adding a few drops more of it to the well-mixed liquid, the liquid being rendered clear for this purpose either by filtration or by letting the precipitate settle. If any further precipitate is formed, the whole of the liquid must be well stirred with more of the reagent, and the clear filtrate must then be again tested in the same way. This process is repeated until no further precipitate is caused by the addition of the Group-reagent.

In certain cases this procedure is rendered unnecessary, since the presence of an excess of the reagent is detectable by its smell, after the solution and the reagent have been well mixed, and the air above the liquid has been blown out. This is the case with H_2S and with AmOH. The presence of an excess of a coloured reagent may usually be seen by the colour of the filtrate from the well-mixed liquid, as in the case of yellow Am_2S. If, however, an acid or an alkaline substance is directed to be added in excess, the student should always prove the presence of an excess by the use of test-papers on the well-mixed liquid.

1207. **Washing Group-precipitates.**—Before a Group-precipitate is examined, it is necessary that it should be washed until it is free from adhering solution (45–47). This must also be done in the separations by filtration which are described in the Group-Tables. If the washing has not been satisfactorily carried out, many complications may arise.

1208. **Evaporation before Precipitating Group III.**—Certain organic substances hinder or prevent the precipitation of the metals of Group III.A. by AmOH. These substances will usually have been already detected in the Preliminary Examination. If they have been detected, it is necessary to destroy them by evaporation and ignition before proceeding to precipitate Group III.

Evaporation to dryness and gentle ignition of the residue are also necessary in order to separate SiO_2 (646), since if this remained in solution it might be mistaken for $Al(OH)_3$. The process also decomposes borates and fluorides.

But if organic substances, borates, fluorides, and silicates are known to be absent, this evaporation is unnecessary, and it is sufficient to boil the filtrate from Group II. until it has no smell of H_2S ; a few drops of strong HNO_3 or of H_2O_2 are then added, and the boiling is continued for several minutes, in order to completely remove H_2S and to convert ferrous salts into ferric salts.

1209. **The Separation of the Sub-groups III.A. and III.B.** from one another, by the method which is given in the General

Table (1235), is seldom complete. For an account of more exact methods, the student is referred to paragraphs 1290 *et seq.*

The method of examining the precipitate in Group III. may also be influenced by the presence of a phosphate in the solution: the change of procedure, and the causes which give rise to it, are explained in paragraph 1292.

1210. **General Remarks.**—It will be seen that the full course of analysis is so arranged that it serves not only to detect what is present in a substance, but also to prove that all else is absent. This is usually the object in view when the analysis of an unknown substance is undertaken.

The process of analysis may in some cases be shortened by using separate portions of the solution for each Group and test. The plan which is recommended in the General Table, of working throughout with the whole of the solution, is however preferable; since, as has been already stated (1202), this procedure usually enables the analyst to form an opinion as to the relative quantities of many constituents of the substance, and this is usually important.

Attention may be drawn to the extreme importance of the spectroscope for rapidly discovering certain substances, especially when they are present in minute quantity only (67).

The acid-radicles cannot be satisfactorily separated into Groups by precipitants as has been indicated for the metals: hence those acid-radicles which cannot be detected by the Preliminary Examinations (1218–1228) have to be found by the application of special tests.

An Example of the Entry of the Results of an Analysis is given in paragraph 1347; it will be seen that the form adopted is that of the Analytical Tables.

A list of Substances suitable for Analysis is given in paragraphs 1415–1419.

The student will do well at first to gain experience in the analysis of easy mixtures, which are completely soluble in HCl and contain no cyanogen, organic salts, silicates, borates, fluorides, or phosphates precipitable in the Third Group. The analysis of such substances will be simple, since it will be unnecessary to evaporate the filtrate from the Second Group to dryness, or to follow any special method of precipitating and examining Group III.

When the ordinary course of analysis has been mastered, the analysis of substances, in which the above complications exist, should be attempted: and finally minerals, water residues, and artificial products and by-products should be analysed, in which minute traces of their constituents should be carefully looked for.

GENERAL COURSE OF ANALYSIS FOR SOLID AND LIQUID SUBSTANCES

The analytical procedure may be influenced by the presence in a substance of *cyanogen* or of a *silicate*. Unless these are known to be absent, it is therefore well to make the tests described in paragraphs 1211, 1212 on small portions of the substance.

1211. **Cyanogen Test.**—A small portion of the substance is subjected to the tests for cyanogen, known as the "Prussian-blue" and the thiocyanate tests and described in paragraphs 692, 694. If cyanogen is detected refer to paragraphs 1316 *et seq.*, for a description of the preparation of the solution and of the method of analysis.

If cyanogen is not present, the substance is examined by paragraphs 1213 and 1214 if it is a liquid, and by paragraphs 1215 *et seq.*, if it is a solid.

1212. **Silicate Test.**—Silicate is tested for by fusing some of the finely-powdered substance in a bead of microcosmic salt (648). If a liquid is being examined, a portion is evaporated to dryness, and the residue is fused into the bead. If silicate is present, and solution of the substance by acids is found impossible (1229), it may be necessary to refer to paragraph 1312.

I. THE SUBSTANCE FOR ANALYSIS IS A LIQUID.

1213. **Reaction to Test-paper.**—Test the liquid with blue litmus-paper and with turmeric-paper (52): one of the following results will be obtained :—

1. **It is Neutral,** not changing the colour of either paper ; this shows the absence of acids and alkalis, and of salts with acid or alkaline reaction. The salts of Ag and Mg and certain salts of Am, Na, K, Li, Ba, Ca, and Sr are the only neutral soluble salts.
2. **It is Acid,** turning *blue* litmus *red* : this shows the presence of an acid or of a salt with acid reaction.
3. **It is Alkaline,** turning turmeric *brown,* and indicating the presence of Am, Na, K, Li, Ba, Sr, or Ca as hydroxide, or of a salt with alkaline reaction.

1214. **Test for Dissolved Solid.**—Evaporate a few drops of the liquid upon platinum-foil, thin glass, or porcelain, smelling it occasionally :—

1. **A Residue is left.**—Note the colour of the liquid (1216) : test a small portion for NH_4 by boiling it with excess of KOH (1218 *Confy.*), and then evaporate a portion of the solution just to dryness in a porcelain dish, without heating the substance after it is dry, and examine the residue by the Preliminary Tables for Metals and Acid-radicles (1218–1228). Examine the larger part of the solution for Metals by the General Table (1235), paying attention to paragraph 1236 : reserve the rest of the solution for the Examination for Acid-radicles by paragraphs 1225 and 1268 *et seq.*

2. **No Residue is left.**—The liquid must consist of some volatile substance, probably of water. This is either pure, or it contains certain gases or volatile substances, such as $(NH_4)_2CO_3$, CO_2, NH_3, HCl, Br, H_2O_2. These may be detected by their smell, by the action of the liquid on litmus-paper, or by special tests (1201, 624–630).

II. THE SUBSTANCE FOR ANALYSIS IS A SOLID.

1215. Examine the General Properties of the Substance.

If the substance is **lustrous and metallic**, refer to paragraph 1299 for the method of analysis; if it is non-metallic in appearance, proceed to make a preliminary examination of it as follows.

Note down anything that can be learned about the physical properties of the substance by the use of the senses aided by a lens or microscope, and by a magnetised penknife-blade.

Note especially whether the substance consists of more or less sparkling particles with similar geometrical shape, when it is said to be **crystalline**; or whether the particles are irregular in shape and **amorphous.**

Also test its **hardness**, by ascertaining whether the substance is readily powdered, or easily scratched with the point of a penknife.

If the particles are sufficiently large, and especially if they are crystalline minerals (1419), ascertain the degree of hardness more carefully, since this will be of use in identifying the substance. Very soft minerals, such as talc and steatite, can be scratched and marked by the thumb-nail: harder substances, such as cryolite or cinnabar, are not affected by the thumb-nail but may be scratched by a bronze coin: still harder minerals, such as apatite and fluorspar, can only be scratched by a penknife: very hard substances, such as quartz, cannot be scratched by a knife, but the knife produces a stain-mark of steel upon their surface.

Try whether the substance is **magnetic** by immersing the tip of a magnetised blade into the fine powder, and seeing whether its particles are attracted. Fe and certain of its compounds are the most powerfully magnetic bodies known, but Mn, Ni, Co and certain of their compounds are also magnetic.

1216. Note also whether the substance possesses any characteristic **smell** or **colour.** The following are some of the more commonly occurring coloured compounds :—

Blue : hydrated cupric salts, and anhydrous cobalt salts.

Green : certain $\bar{Fe}$ salts are pale green; $CuCl_2$, salts of Ni, manganates and certain compounds of Cr, are intense green.

Yellow : HgO, PbI_2, As_2S_3, CdS, SnS_2, chromates, $Fe^{\cdots}$-salts.

Red : HgO, HgI_2, HgS, Pb_3O_4; dichromates are orange-red; permanganates are usually reddish-purple.

Pink: salts of Mn are delicate pink; hydrated salts of Co are reddish-pink.
Brown: Fe_2O_3, PbO_2; PbO and CdO are light brown.
Black: CuO, MnO_2, Sb_2S_3, FeS, Fe_3O_4.
White: anhydrous salts of Cu and Fe, and many other substances.
Colourless: a large number of colourless substances are known; these, as well as many of the faintly coloured bodies, yield *white* powders when they are crushed.

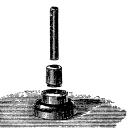
1217. **Reduction to fine powder.**—After the above examination has been completed, the solid substance is reduced to the finest powder possible, by rubbing it in the mortar.

An ordinary Wedgwood mortar may be used for powdering substances which are fairly soft; but hard rocks and minerals frequently require to be first crushed in a clean bright steel percussion mortar (Fig. 63) by blows of a hammer, and are afterwards pulverised *by trituration only* in an agate mortar.

FIG. 63.

STEEL MORTAR.

It must be understood that the subsequent chemical examination is very greatly facilitated if the substance has been carefully reduced to an impalpable powder, which does not feel gritty when it is rubbed beneath the pestle or between the fingers.

A portion of this powder is submitted to the further tests which are described in the following Preliminary Examinations for Metals (1218) and for Acid-radicles (1225), using a small separate portion for each test: the remainder is reserved for the fuller method of examination in solution (1229 *et seq.*).

PRELIMINARY EXAMINATION FOR METALS.

If the substance for analysis is a liquid, part of it may be evaporated to dryness, and subjected to the following tests:—

Experiment.	Observation.	Inference.
1218. Exp. I.—Heat a little of the substance in a small test-tube or ignition-tube.	**A. The substance does not change.** The substances described under B. below are probably absent, or present only in very small quantity.	Absence of *organic* substances which blacken and give off a smell of burning; of *volatile* substances which sublime; of substances which are altered by ignition; and of *water* combined with or absorbed by the substance, which would be evolved as steam and form drops on the side of the tube.
	B. The substance changes.	
	1. *It changes colour*:—	
	Yellow, hot. | *white*, cold.	ZnO.
	Yellow, brown „ | *yellow* „	PbO.
	Yellow-brown „ | *yellow* „	SnO_2 or Bi_2O_3.
	Dark red or *black* „ | *red-brown* „	Fe_2O_3.
	The substance blackens—	
	a. Emitting a smell of burning. The black carbon may be burnt off by strongly heating on platinum-foil with the blow-pipe flame. (Exp. 21, page 39)	Presence of organic matter.
	Smell of acetone.	An acetate.
	Smell of burning sugar.	A tartrate, etc.
	b. Emitting no smell of burning. The colour is not removed by ignition as under *a*.	Probable presence of Co-, Mn-, or -Cu salts.
	2. *It fuses, and becomes solid again on cooling.*	Alkali-salts or certain alkaline earth salts.
	3. *It sublimes.*	Compounds of Am, As, Hg; or free S or I.
Confirmatory. — The sublimate is carefully examined, if necessary with the aid of a lens.	White, crystalline, sparkling sublimate.	$HgCl_2$, As_4O_6.
	White, non-crystalline sublimate.	Probably Am-salt.
	Black sublimate, becoming red when rubbed.	HgS.
	Yellow sublimate.	As_2S_3. HgI_2, becomes scarlet when rubbed.
	Sublimate of reddish drops, which are yellow when cold.	S free, or from certain polysulphides.
	Violet vapour, cooling to blackish crystals.	Presence of I.
Confirmatory. — Heat another portion of the substance, mixed with about three times as much Na_2CO_3 in fine dry powder and a little KCN, in an ignition-tube (140).	Grey mirror, which, when rubbed with a splinter of wood or a glass rod, or when examined by a lens, is seen to consist of globules of Hg.	Presence of Hg.
	Blackish-brown shining mirror, and smell of garlic, no globules.	Presence of As.
Confirmatory. — Pour strong KOH-solution upon the substance and heat to boiling; or mix the substance with soda-lime in a mortar, and moisten and heat.	NH_3 is given off, known by its smell and by turning moist red litmus-paper blue or turmeric-paper brown.	Presence of NH_4.
	4. *The substance gives off water.*	Presence of water, absorbed or combined.
	It fuses first, then gives off water, and again becomes solid if the heating is continued.	Water of crystallisation.
	It swells up considerably while it is giving off water.	Borax and certain borates, alums, and phosphates.

Experiment.	Observation.	Inference.
Confirmatory. — Examine the drops of water on the sides of the tube with blue and red litmus-papers.	The water is alkaline. The water is acid.	Probably NH_4-compounds. Presence of salts of the volatile acids, *e.g.* HNO_3, HCl, H_2SO_4.
	5. *Gas or vapour is given off.**	
Confirmatory. — Introduce a burning splinter of wood into the tube.	*a. It is without smell.* It burns more brightly, and if introduced with a spark at the end is inflamed.	O (from chlorate, nitrate, peroxide, etc.); or N_2O.
Confirmatory. — Introduce a glass rod, moistened with lime-water, into the tube.	The flame is extinguished. The lime-water turns milky. The lime-water does not turn milky, but the flame is extinguished.	CO_2 or N. CO_2 from carbonate, oxalate, etc. N from $AmNO_2$ probably.
Confirmatory. — Introduce a glass rod or slip of paper moistened with $K_2Cr_2O_7$-solution.	*b. The gas or vapour has a smell.* Smell of burning S. The $K_2Cr_2O_7$ turns green; moist blue litmus is also reddened by the gas.	SO_2 from combustion of free S, or from acid sulphites, thiosulphates, reduction of sulphates or oxidation of sulphides.
	Reddish-brown nitrous fumes are given off, known by their peculiar smell, and by not colouring starch paste orange red.	Nitrates of heavy metals, *e.g.* of Pb, Bi, Hg.
Confirmatory. — Introduce a glass rod carrying a piece of moist litmus.	Smell resembling Cl :— Yellowish gas, which bleaches moist litmus.	Cl from certain chlorides.
Confirmatory. — Introduce a glass rod with moist starch-powder on its end.	Brown vapour, which colours the moist starch-powder orange red. Violet vapour, which colours starch-solution blue (552, *Note* 1). NH_3 is smelt.	Br from certain bromides. I, free or from certain iodides. NH_4- or cyanogen-compounds.
	c. The gas can be ignited, and burns at the mouth of the tube with a :— Pale *yellowish green* flame, more or less explosive. Bright *white* flame, producing white fumes; the unburnt gas smells of garlic. *Peach-blossom coloured* flame.	NH_3 probably from strongly heated NH_4NO_3. PH_3, probably from a phosphite or hypophosphite. C_2N_2 from a cyanide, probably from $HgCy_2$.
1219. Exp. II.—Dip a moistened loop of platinum wire, which gives no colour to the Bunsen-flame, into the substance, and hold the loop with the adhering powder near the top of the Bunsen-flame, or in the inner blowpipe-flame. Then moisten with a drop of strong HCl and heat again. Continue the heating until no further change occurs in the colour of the flame.	A. **The substance colours the flame :—** 1. *Intense yellow.* Examine the flame through the indigo-prism; a crimson colour is seen. 2. *Pale lilac,* crimson through the indigo-prism. 3. *Yellowish green.* 4. *Crimson,* same through the indigo-prism.	Na. Presence of K, Sr, Li. The spectroscope is decisive (65). K. Ba probably. Sr, Li.

* This will usually be shown by effervescence of the substance; if the gas or vapour is not detected by its colour or smell, it can only be found on testing for it specially by the confirmatory tests below.

Experiment.	Observation.	Inference.
The flame coloration should also be carefully examined by means of the spectroscope (64, 65).	5. *Orange red*, dingy green through the indigo-prism.	Ca.
	6. *Bright green.*	Cu or B_2O_3.
Note. If silicic acid is present, the colorations for K and Na usually show only after ignition of the powdered substance with powdered $CaSO_4$.	A blue colour is seen after moistening with strong HCl.	Cu.
	7. *Blue* { *Intense.*	$CuCl_2$, $CuBr_2$.
	{ *Livid.*	As, Sb, Pb, $HgCl_2$, $ZnCl_2$, $SnCl_2$.
1220. Exp. III. — Heat the finely-powdered substance, in a small cavity scooped in a piece of wood-charcoal, in the blowpipe-flame.	**A. The substance decrepitates or crackles.**	NaCl and certain other crystalline salts.
	B. The substance deflagrates, or causes the charcoal to burn rapidly.	Chlorate, nitrate, etc.
	C. The substance fuses easily, and is absorbed by the charcoal, or forms a liquid bead.	Salts of alkalis and certain salts of the alkaline earths.
	D. An infusible residue is left on the charcoal: see 1, 2, 3, below:—	
	1. *The residue is white and very luminous.*	Probably BaO, SrO, CaO, MgO, Al_2O_3, ZnO, or SiO_2.
Confirmatory. — Detach a portion of the cool residue from the charcoal, place it upon a piece of red litmus-paper, and moisten with a drop of water.	The paper turns blue, showing the residue to be alkaline.	BaO, SrO, CaO, and possibly MgO.
Confirmatory. — Moisten the residue on the charcoal when cool with several drops of $Co(NO_3)_2$-solution, and heat again strongly in the outer blowpipe-flame.	A *blue* residue, the colour of which does not disappear with intense heat.	Al_2O_3, and some phosphates, arsenates, silicates, and borates.
	A *pink* residue.	MgO.
	A *green* residue.	ZnO, or possibly Sn.
	2. *The residue is coloured.* Colour of bead:	
Confirmatory. — Heat a small quantity of the substance in a clear colourless borax bead, first in the outer, then in the inner blowpipe-flame.	In outer flame. — In inner flame.	
	Green, hot, and *blue*, cold. — *Colourless*, or *red*, cold.	Cu.
	Blue, hot and cold. — *Blue*, hot and cold.	Co.
	Violet, hot, and *yellow*, cold. — *Grey* or *opaque*.	Ni.
	Brown-red, hot: *yellow*, cold. — *Olive green*, hot and cold.	Fe.
	Green, hot and cold. — *Green*, hot and cold.	Cr. } See following *Confirmatory* test.
	Reddish purple, hot and cold. — *Colourless*, hot and cold.	Mn. }
Confirmatory. — The presence of Mn and Cr. may be confirmed by fusing the substance with Na_2CO_3 and KNO_3 or Na_2O_2, on platinum-foil (Exp. 25, 56).	*Light-yellow* mass on cooling.	Cr.
	Blue-green mass on cooling.	Mn. (See 1222.)
	3. *The residue is coloured, or metallic scales or globules are seen.*	
Confirmatory. — Heat also some of the substance, mixed or covered with powdered KCN and Na_2CO_3 or $K_2C_2O_4$ on charcoal in the inner blowpipe-flame.	The substance is reduced to the metallic state (1223):—	Au, Ag, Cu, Pb, Sn, Sb, Bi; [Co, Ni, Fe, Mn, form grey powders].
	a. Without incrustation.	Au, Ag, Cu, Co, Ni, Fe, Mn, Sn.
	Brilliant white metal.	Ag, Sn: Ni if hard.
	Yellow metal.	Au.

Experiment.	Observation.		Inference.
	Red scales or globules.		Cu.
	Grey powder, attracted by a magnetised knife-blade (1223).		Fe, Co, Ni, Mn.
	b. With incrustation.		
	Globules.	Incrustation.	
Confirmatory. — Detach several of the globules with the point of a knife, and strike them on the bottom of an inverted mortar with the pestle; if they flatten to a cake they are *malleable*, if crushed to a powder they are *brittle*. Try also if a globule, fixed on the point of a knife, marks paper.	*White, malleable,* not marking paper.	None, or very slight.	Sn.
	White, brittle.	*Orange,* hot. *Yellow,* cold.	Bi.
	White, malleable, marking paper.	*Yellow,* hot and cold.	Pb.
	White, brittle, giving white fumes.	*White,* close to substance.	Sb.
Note.—The appearance and malleability of one reduced metal is frequently much altered by the presence of another.	*None.*	*Yellow,* hot. *White,* cold.	Zn.
	None.	*Red-brown,* easily volatilised.	Cd.
	None.	*White,* and white fumes; smell of garlic.	As.
1221. Exp. IV.—Fuse some of the substance, mixed with Na_2CO_3, on charcoal in the inner blowpipe-flame produced from a spirit-lamp, or from a gas-flame known to be free from S: remove the fused mass when cold, place it on a bright silver coin, moisten with a drop of water, and let stand for several minutes.	On rinsing off the substance, the coin is found to be stained black (481). Also if a drop of HCl is placed upon the mass, a smell of H_2S is perceived and lead-paper is blackened (480).		Presence of S, free or combined. *Note.* — Since this reaction serves to detect S and sulphur-acid-radicles, it more properly belongs to the Preliminary Examination for acid-radicles: it is, however, best tried here.

NOTES TO THE PRECEDING PRELIMINARY TABLE.

1222. The green colour produced by Mn conceals the yellow colour due to Cr; on boiling the residue with water it gives a pink or purple solution, the colour of which is best seen on filtering: this colour is due to the formation of $KMnO_4$, and shows Mn to be present. On acidifying this solution with H$\bar{A}$ and boiling again for several minutes, the purple colour is destroyed; and on filtering, the yellow colour due to Cr is seen: the presence of Cr may be further confirmed by the formation of a yellow precipitate in the acid solution on addition of Pb$\bar{A}_2$-solution.

1223. The metal is best separated and examined by detaching the mass when cold from the charcoal, and crushing it in a mortar or on a watch-glass with a little water, letting stand for a short time, and then quickly pouring off the water down a glass rod or pestle which is wetted and pressed against its edge; by several times repeating this operation, the heavier metallic particles alone are left in the mortar or watch-glass (61).

The particles of metal may be dissolved at once in dilute HCl or HNO_3

and special tests may be applied to the solution for the identification of the metal.

1224. General Note.—When the substance to be examined contains several bodies, they frequently more or less mask one another's reactions: thus Co if mixed with Fe will give a borax bead which is green whilst hot and blue when cold, thus resembling Cu, but differing in remaining blue in the inner flame.

Hence the composition of many complex mixtures is only roughly indicated by the Preliminary Examination, and must be confirmed and established in the wet way, or in solution. Many substances, more particularly minerals, however, can be completely analysed by a careful Preliminary Examination.

PRELIMINARY EXAMINATION FOR ACID-RADICLES.

1225. The substance is required for this examination in the state of powder or of *strong* solution.

If the substance given for analysis is a solution, part of it may be evaporated to dryness : the dry residue is then finely powdered and subjected to the following tests. If several acid-radicles and metals are present, the reactions may be more or less perfectly concealed or altered, hence failure in obtaining a certain reaction does not in all cases necessarily prove the absence of the corresponding acid-radicle.

Experiment.	Observation.	Inference.
1226. Exp. I.—Treat some of the substance with dilute HCl and note the result, then heat moderately.	*One or more of the following gases may be evolved :—*	
	A colourless inflammable gas, free from smell.	Hydrogen or methane from a metal or metal carbide.
	A colourless gas without smell, which turns milky a drop of lime-water on the end of a glass-rod (474).	CO_2 from a carbonate.
	A gas of suffocating smell, which turns a drop of $K_2Cr_2O_7$ solution green (489).	SO_2 from a sulphite, or from a sulphate in the presence of As_4O_6 or other reducing substance. See 1288.
	Yellow S separates, and SO_2 is evolved (494).	SO_2 and S from a thiosulphate. See 1288.
	A gas with fetid odour, which blackens a drop of PbA_2 solution, or a piece of lead-paper (480).	H_2S from a sulphide ; or possibly from a sulphite or thiosulphate, if Zn or other reducing agent is present. See 1288.
	Reddish fumes.	From a nitrite.
	A yellowish-green gas of suffocating smell, which bleaches moist litmus-paper, is evolved (499) :—	
	a. In the cold ; and also evolved on adding $H\bar{A}$.	Cl from hypochlorite.
	b. Only when heated.	Cl from action of HCl on oxidising substances, *e.g.* MnO_2, chromate, nitrate, chlorate, etc.
	A colourless gas, smelling of bitter almonds.	HCN from a cyanide.
Dip into the above HCl-solution a strip of turmeric-paper.	On drying this paper at a gentle heat, it becomes reddish-brown (634).	Presence of a borate.
1227. Exp. II. — Heat another portion of the substance gently with strong H_2SO_4. No attention need be paid to the gases evolved in Exp. I. (1226).	1. A gas is evolved with pungent smell, which fumes in the air, and renders milky a drop of $AgNO_3$-solution made acid with HNO_3.	HCl, HBr, HI, HF * from chloride, bromide, iodide, or fluoride. Bromide also evolves brown Br-vapour, and iodide purple I-vapour (see below).
Confirmatory. — Mix some of the substance with MnO_2 *free from chloride* (541), add strong H_2SO_4 and warm.	A *yellow* gas is given off with strong smell, which bleaches moist litmus-paper.	Probably Cl from chloride.
	Brown vapour is given off, which colours a little moist starch-powder orange-red.	Br from bromide.
	Violet vapour is given off, which colours a drop of starch-paste blue (554).	I from [illegible]ide.

* HF acts upon the glass, and the SiF_4 formed renders the drop milky with SiO_2, but the glass is etched (2, page 258).

Experiment.	Observation.	Inference.
	2. A heavy fuming suffocating gas is evolved, and the liquid behaves as if the glass were greasy: on rinsing out the tube, and drying it thoroughly, the inside is seen to be corroded and dimmed.	HF from fluoride: confirm by 654. The HF acting upon the silica of the glass evolves SiF_4, which is detected by holding a moistened glass rod in the gas: SiO_2 will be deposited as a gelatinous film upon it (655).
Confirmatory.—Drop into the hot liquid a few small pieces of copper. If no brown fumes are seen proceed to the next test.	3. The acid fumes are reddish, usually seen only on *heating* after adding a few fragments of Cu.	Presence of nitrate. If iodide is present it must usually be separated by $CuSO_4$ (553) before a nitrate can be detected.
Confirmatory. — Boil some of the solid substance with water, or take some of the liquid; cool, add about twice as much strong H_2SO_4, cool, and pour cold solution of $FeSO_4$ carefully in upon the top of the acid liquid.	A dark brown ring or layer forms upon the surface of the acid, either at once or on cooling the liquid by immersing the test-tube in cold water. [Refer to *Note*, 1276.]	Presence of nitrate.
	4. The acid is coloured reddish-yellow, and a yellow gas is evolved which smells like Cl and bleaches litmus: on heating the acid explosion or crackling occurs. Confirm by 519.	Presence of chlorate. *Note.*—For the detection of nitrate or hypochlorite with the chlorate see 524, 1287, 1286.
	5. The substance changes from yellow to green, O being evolved, as is shown by a glowing taper.	Presence of chromate.
	6. Yellowish green gas, with suffocating smell, which bleaches moist litmus.	Cl from a hypochlorite (detected already in 1226), or from a chloride in presence of MnO_2, etc.
	7. The same gas as in 6, but coloured *reddish brown* by nitrous fumes: or coloured reddish brown by $CrOCl_2$.	A chloride in presence of a nitrate or nitrite. A chloride in presence of a chromate.
	8. Substance does not blacken, but evolves CO which burns with a blue flame, and CO_2 which turns a drop of lime-water milky.	Presence of oxalate.
	9. Substance blackens, and SO_2 is smelt.	Presence of tartrate.
	10. A smell of acetic acid or vinegar is noticed.	HA from acetate.
Confirmatory. — Add a little alcohol to the substance and heat with H_2SO_4.	Strong fragrant odour.	Ethyl acetate from an acetate.

NOTE ON THE PRECEDING TABLE.

1228. The S present in sulphides which are not decomposed by dilute HCl (1226), is detected by fusing the powdered substance with two or three times as much fusion mixture ($Na_2CO_3 + K_2CO_3$) in a covered crucible, boiling with a little water, and placing a drop of the solution upon a bright silver coin, [illegible] a dark stain will be produced; or by adding excess of an acid to the solution, when H_2S will be evolved. Smaller quantities of S may be detected by the formation of a black colour or precipitate on adding PbA_2 solution to the solution of the fused mass.

EXAMINATION FOR METALS IN THE WET WAY.

After the Preliminary Examination of the solid substance has been completed, a portion of the substance is dissolved (1229), and the solution is submitted to the systematic examination, which commences at paragraph 1235. This is often termed "The Examination in the Wet Way."

PROCESS OF SOLUTION.

1229. The liquids which are used as solvents for solid substances are (*a*) water, (*b*) hydrochloric acid, (*c*) nitric acid, and (*d*) aqua regia. The majority of substances dissolve either in water or in HCl, a few require HNO_3, but the use of aqua regia is rarely necessary. The method of applying these solvents to the preparation of the solution of a solid substance is stated below.

Introduce a portion of the solid substance, reduced to an impalpable powder (1217), into a flask (Fig. 21B, page 20) or boiling-tube with distilled water, and heat the water to boiling (1232): if the substance dissolves entirely, proceed to 1235.

If the powder does not dissolve, allow the liquid to stand until the undissolved portion has in great part settled, then decant through a filter: the filtrate is Solution I.:—

Residue in flask: boil with dilute HCl (1232), allow any residue to settle, decant through the filter used above (1233); repeat this process and finally boil the residue with strong HCl, let settle, and decant through the filter:—			
Filtrate is	*Residue:* heat with dilute, then with strong HNO_3 (1234) as was directed above for HCl, and decant through the filter:—		
	Filtrate is	*Residue* may be warmed for a short time with a mixture of strong HNO_3 (1234) with three times as much HCl; if this does not dissolve it, dilute and decant the acid mixture through the filter:—	
		Filtrate is	*Residue:* wash well with water, dry, and examine as is directed for substances insoluble in water and acids (1306 *et seq.*).
Solution II.	Solution III.	Solution IV.	

1230. Solutions I., II., III., IV. need not be examined separately. Add to I. a few drops of dilute HNO_3, and if no precipitate is pro-

duced (1236) acidify it with HCl; add also some HCl to Solution III. Any precipitate caused by HCl in these solutions is filtered off and examined by Table I. (1250). The Solutions I., II., III., IV. are then mixed together, and any precipitate produced by mixing them is examined by paragraphs 1306 *et seq.* as an insoluble substance.

It is best to boil down Solutions III. and IV. considerably, in order to get rid of most of the HNO_3 which they contain, before they are mixed with Solutions I. and II.

The mixed Solutions are then examined by 1235.

1231. If a complex solid mixture is given for analysis, and the only object is to obtain a solution as rapidly as possible, the substance may be at once boiled with aqua regia for a few minutes, then diluted and filtered. The undissolved residue is examined as a substance insoluble in water and acids (1036, *et seq.*). The filtrate is evaporated nearly to dryness, dilute HCl is added, and the solution is examined by the General Table (1235).

1232. **Any Changes** which occur when the substance is treated with water or with HCl should be noted down. Notice especially whether any gases are given off.

Water may cause the evolution of oxygen from peroxides of the alkali- or alkaline earth-metals, of hydrocarbons from metallic carbides, of acetylene from calcium carbide, carbon dioxide from bicarbonates, hydrogen sulphide or hydrogen phosphide from certain metallic sulphides or phosphides.

Many of the gases evolved by treatment with HCl may be at once recognised by their smell; but a closer examination may be neglected, as these gases will have been already obtained in the Preliminary Examination for Acid-radicles (1226).

If the gases are evolved from the aqueous solution when HCl is added, or when the HCl and aqueous solutions are mixed, the corresponding acid-radicles must have been present in salts soluble in water, probably salts of alkali-metals. If the gases are evolved when the residue insoluble in water is treated with HCl, the acid radicles were present in salts insoluble in water.

1233. **When the hot HCl solution is cooled,** crystals may separate. These usually consist of $PbCl_2$, rarely of $BaCl_2$. The crystals should be filtered off and dissolved in a little boiling water. Ba is easily found by the flame-coloration which is given by the solution (406). The formation of a *bright yellow* precipitate, when a drop of K_2CrO_4 is added to the solution, proves the *Presence of Pb*: Ba gives only a *pale yellow* precipitate.

If Pb has been found, and a residue is left after the original substance has been treated with HCl, the residue may consist of $PbCl_2$;

this substance may be dissolved by boiling it with water, and the use of HNO_3 may be avoided (1234).

1234. **HNO_3 seldom requires to be used** in dissolving a substance. This acid should be employed, when necessary, only in very small quantity, since it decomposes the group-reagent H_2S with separation of S unless the solution is dilute and cold (1239): the presence of HNO_3 may accordingly delay or prevent the precipitation of Group II.

The solubility of the compounds of the metals in various solvents is given in the Table of Solubilities (1264). A reference to this Table will often be of advantage after the metals and acid-radicles have been detected by the preliminary examinations, and the solubility of the substance has been determined by the preceding directions, as it will serve to indicate what the substance may contain.

GENERAL TABLE FOR SEPARATION OF METALS

1235. If the substance for analysis is a liquid with *neutral* or *alkaline* reaction, examined as is directed below.

In this Table, and in the Group-Tables which follow, it has been supposed that be produced when the reagent is added for its detection; and hence no filtration

The "original solution" referred to below is the solution of the substance if

<table>
<tr><td colspan="3">Add to the greater part of the "original solution" HCl; if any precipitate is produced, continue to</td></tr>
<tr><td rowspan="2">The precipitate may contain—

$PbCl_2$—white.
$AgCl$—white.
Hg_2Cl_2—white.
(See 1238.)

Examine the precipitate by Table I. (1250).

———

Note.—When the hot HCl-solution is cooled, $PbCl_2$ often separates in colourless crystals.
The absence of Pb is not proved, if it is not precipitated in this group, as $PbCl_2$ is somewhat soluble, and Pb may therefore be found only in Group II.</td><td colspan="2">The filtrate or solution, which must give no further precipitate on unless it is already dilute, and saturated with H_2S by passing the precipitate the metals (1241): it is then filtered:—</td></tr>
<tr><td>The precipitate may contain—

HgS—black
PbS—black
Bi_2S_3—black
CuS—black
CdS—yellow
} Insoluble in KOH and in Am_2S.

SnS—brown
SnS_2—yellow
Sb_2S_3—orange
As_2S_3—yellow
[Au_2S_3—black]
[PtS_2—black]
} Soluble in KOH and in Am_2S.

Examine the precipitate at once by Table II. (1252).

———

Note 1.—Any precipitate formed on boiling the filtrate must be added to the above (1244).

Note 2.—Unless the liquid has been sufficiently diluted some of the above metals may be afterwards precipitated by Am_2S in Group III., and cause much confusion.</td><td>The solution or filtrate is diluted precipitated: as soon as H_2S to smell of H_2S (1244), a little
But if an organic substance, gently ignited in the dish. When undissolved residue is filtered

Add a few drops of this acid solution of Phosphate; if no precipitate

Add to the rest of the HCl-solution which may form, as quickly as precipitate is produced by AmOH

[Note.—Refer to 1294,

The precipitate may contain—

$Al(OH)_3$—almost colourless.
$Cr(OH)_3$—light green.
$Fe(OH)_3$—reddish brown.

Examine the precipitate by Table III.A. (1255).</td></tr>
</table>

NOTES ON THE

1236. If the liquid under examination is alkaline or neutral in reaction, HNO_3 commenced. A change of colour from green to purple indicates the *Presence of* by the General Table; if a precipitate is produced, more HNO_3 is added, and is examined by the General Table, commencing with the addition of HCl.

A precipitate which is caused and not dissolved by HNO_3 may be finely divided from a thiosulphate; this precipitate may be recognised by its colour, and by not There may also be precipitated H_2SiO_3 (gelatinous, almost colourless), SnO_2 or Sb_2S_3 (orange).

A full examination of this precipitate for all that it may contain may be made it; any insoluble residue which remains is then examined as a substance insoluble

INTO GROUPS BY GROUP-REAGENTS.

it requires special treatment (1236); if its reaction is *acid*, it may be at once

all metals are present: if a metal or group of metals is absent, no precipitate will
is necessary, the solution being treated as a filtrate.
a solid, or the substance itself if a liquid, to which no reagent has been added.

add HCl as long as it causes any further precipitate, warm and filter :—

addition of several drops of HCl, is boiled down if necessary (1239): it is then diluted with water (1241);
gas through the solution (1374) for several minutes; or sufficient H_2S-water is added to dilute and

and H_2S is passed again into it, or more H_2S-water is added, to make sure that Group II. is completely
produces no further precipitate the clear solution or filtrate is boiled in a porcelain dish until it ceases
strong HNO_3 or Br-water is then added, and the liquid is boiled.
borate, fluoride or silicate, may be present the liquid must be evaporated to dryness and the residue
the dish is cool, a little strong HCl is poured upon the residue and heated, then water is added; any
off (1245).

to some $AmHMoO_4$-solution in a test-tube, and warm gently; a yellow precipitate shows the *Presence*
is formed with $AmHMoO_4$, *Phosphate is absent.*

AmCl, heat it to boiling, then add AmOH in slight excess, boil again, and filter off any precipitate
possible, keeping the funnel closely covered with a glass plate (1246): if phosphate is present and a
refer to Tables (1256); if phosphate is absent proceed as is directed below :—

et seq., for further directions for precipitating and examining Groups III.A. and III.B.]

Add to the filtrate or solution, which may be coloured (1247), yellow Am_2S in excess, boil and filter :—

The precipitate may contain—	Add to the filtrate or solution, which must be distinctly yellow or brown (1248), Am_2CO_3, warm gently and filter :—	
ZnS—*white.* MnS—*light-pink.* CoS—*black.* NiS—*black.* Examine this precipitate *at once* by Table III.B. (1257).	The precipitate (1249) may contain— $BaCO_3$—*white.* $SrCO_3$—*white.* $CaCO_3$—*white.* Examine the precipitate by Table IV. (1260).	The filtrate may contain Mg, K, Na, Li. Examine by Table V. (1263).

GENERAL TABLE.

must be added in slight excess, before the examination by the General Table i
Manganate (609, 610); but if no precipitate forms, the liquid is at once examine
the liquid is heated, and if a precipitate still remains, it is filtered off and the filtrat

sulphur, which separates as a *white* powder from a sulphide, and as a *yellow* powde
being separable by standing or filtration; it may be disregarded.
metastannic acid (1237), Sb_2O_5, AgCl (all three white), SnS_2, As_2S_3 (both yellow)

by boiling the precipitate with aqua regia, and then diluting the liquid and filterin
in water and acids (1306); the aqua regia solution is added to the filtrate fro
is caused by mixing these solutions is examined by Table I. (1250).

1237. Metastannic acid is precipitated from the solution of an alkaline metastannate by the addition of an acid. It forms a white precipitate, which becomes *golden-yellow* when it is moistened with $SnCl_2$-solution. It is also recognised by dissolving in the washing-water, and being reprecipitated when the water runs into the acid filtrate.

1238. It must be remembered that *strong* HCl also precipitates a strong solution of a barium salt. This precipitate, however, is readily dissolved[1] when water is added and the liquid is heated: it is easily distinguished in this way from AgCl and Hg_2Cl_2.

1239. If HNO_3 or aqua regia has been used in dissolving the substance (**1229**, **1234**), or if the solution smells of Cl or SO_2, the liquid should be boiled down considerably, until neither of the above gases is smelt when HCl is added and the liquid is again boiled. The solution is then diluted, and H_2S is passed into it, or H_2S-water is added, at once, whether the dilution has caused a precipitate or not (**1241**).

If As has been detected in the Preliminary Examination, H_2SO_3 should be added, until the liquid smells of SO_2 after it has been boiled for a short time. The liquid is then heated for some time short of boiling until it no longer smells of SO_2. This treatment reduces arsen*ic* and stann*ic* compounds to the arsen*ious* and stann*ous* condition.

In the case of As this reduction is to be recommended, since arsen*ic* compounds are not easily precipitated by H_2S. It is also very desirable to reduce stannic compounds, since SnS_2, unlike SnS, readily runs through the filter, and being yellow in colour may be mistaken for S. It will of course be necessary to try the special tests **184–186** and **201–203** upon the *original solution*, in order to ascertain in which state As and Sn were originally present. If any precipitate, other than white sulphur, is produced by boiling with H_2SO_3, refer to paragraph **1240**.

1240. While the solution is being boiled with H_2SO_3, some H_2SO_4 is usually formed. This acid may partially or completely precipitate Pb, Ba, Sr as white sulphates.

H_2SO_3 may also precipitate Au as a fine powder, which causes the cool liquid to appear blue by transmitted and brown by reflected light; this fine precipitate remains suspended but separates as a black powder when the liquid is boiled.

Examine any precipitate which has been formed by H_2SO_3 by Table G (**1251**).

1241. Dilution with water will cause Bi, Sb, Sn to form white precipitates of their oxychlorides. These precipitates may be disregarded, since H_2S readily converts them into sulphides.

1242. H_2S often produces a fine *white* precipitate of S, which is caused by the presence of certain oxidising substances, such as Cl, HNO_3, $HClO_3$, H_2CrO_4, $HMnO_4$, H_2SO_3, $FeCl_3$ (**1239**). This precipitate is white and is not separable by standing or by filtration; it may be neglected.

Great care, however, must be taken not to mistake SnS_2 for S; it resembles S in running through filter-paper, but differs by being distinctly *yellow* in colour; it may often be coagulated by shaking or heating the liquid.

1243. Certain changes may be observed while H_2S is being passed; they should be carefully noted.

Thus while Pb and Hg are being precipitated by H_2S, the precipitates often show characteristic colours (**103**, **134**).

Also a solution, which is coloured *reddish-yellow* by H_2CrO_4, becomes *green*; a solution, which is coloured *purple* by $HMnO_4$, becomes *colourless*; and a *reddish-yellow* ferric solution becomes a *pale-green* ferrous solution.

Each of these changes is attended by separation of sulphur.

1244. If a yellow precipitate forms when the filtrate or solution which has been saturated with H_2S is boiled, the presence of an arsen*ic* or a stann*ic* compound is indicated.

In this case H_2S should be passed into the boiling liquid, or H_2S-water added, as long as it causes any further precipitate, the precipitation being preceded with advantage by reduction with SO_2 (1239). The precipitate is filtered off and added to any precipitate which has been already obtained by H_2S, and is then examined by Table II. (1252).

1245. SiO_2 and other substances may be present in the insoluble residue which is left after evaporation with HCl.

SiO_2 is distinguished from any other substance by disappearing when it is heated with HF.

Al_2O_3, Fe_2O_3, Cr_2O_3 may remain undissolved by HCl, if they have been rendered difficultly soluble by the ignition to which the residue has been subjected. They can be dissolved by long-continued heating with strong HCl. The solution thus obtained is added to the main solution, which is to be examined for Group III.A. An alternative method consists in fusing the insoluble residue with $KHSO_4$, dissolving the cool mass in water and examining it by Table III.A. (1255).

$BaSO_4$ and $SrSO_4$ may also remain undissolved. They are detected by heating some of the residue strongly for a short time in the inner blowpipe-flame upon a loop of platinum wire, then moistening the loop with a drop of strong HCl, and holding it in the outer part of the Bunsen-flame. Crimson-red flashes, which appear red through the indigo prism, show the presence of Sr; a yellowish-green flame-coloration shows that Ba is present. These flame-colorations should also be examined by the spectroscope (64, 65).

The following is a less rapid method of detecting Ba and Sr. Dry the insoluble residue; fuse it on platinum-foil with three or four times as much Na_2CO_3; allow it to cool, then boil the mass with water until it is disintegrated; filter, wash the residue well upon the filter, and examine it by Table IV. (1260) for Ba and Sr only.

1246. Mn and Zn may accompany the precipitate of $Fe(OH)_3$, $Al(OH)_3$ and $Cr(OH)_3$ in Group III.A.

The precipitation of Mn is partly prevented by keeping the liquid from exposure to the air, after AmOH has been added in excess.

But the further precaution should be taken of dissolving the precipitate, which has been produced by AmOH, in HCl, and reprecipitating it by AmOH; the liquid is then filtered, and the filtrate is added to the filtrate which was originally separated from the Group III.A. precipitate.

This treatment of the precipitate should be repeated several times, if small quantities of Zn or Mn have to be looked for in the presence of Al or Fe.

It is better still to precipitate Groups III.A. and III.B. together (1290), and to examine the precipitate by Tables III.C., III.D. (1295, 1296). See rules given in paragraph 1294.

1247. The filtrate or solution, after the addition of AmCl and AmOH, may be coloured *blue* by Ni, *brown* by Co, or *reddish-violet* by $Cr(OH)_3$, which may have been dissolved by the excess of AmOH.

The $Cr(OH)_3$ alone need be removed before proceeding to examine for the remaining Groups. It is readily separated, as a pale green, flocculent precipitate by boiling the liquid for a short time in a porcelain dish, a little more AmOH being added if the liquid does not smell of NH_3 after it has been boiled for a short time. This precipitate is filtered off, and the filtrate is further examined for Groups III.B., IV., and V. by the General Table (1235).

The coloration of the ammoniacal liquid, which is caused by Ni or Co, is not removed by boiling the liquid: it is simply noted down.

1248. A *greenish colour* may be given to the Am_2S filtrate by a trace of FeS remaining in solution: the FeS will usually be separated as a black precipitate by boiling the liquid: the precipitate may be filtered off, dissolved in HCl and tested for $Fe^{\cdot\cdot}$-salt.

A *brown* or *dark colour* in the filtrate from the Group III.B. precipitate shows that Ni is present, the colour being due to the solution of some of the NiS in the excess of yellow Am_2S; but if Groups III.A.–B. have been precipitated together (1290) the coloration of the filtrate may also be due to $Cr(OH)_3$.

Before proceeding to precipitate Group IV., the dark coloured filtrate should be poured into a porcelain dish and boiled for some time, adding a little water if necessary to prevent evaporation to dryness: when pale-green $Cr(OH)_3$ may separate, leaving a colourless liquid.

If black NiS settles down and leaves a colourless liquid when the lamp is removed for a few minutes, the liquid is passed through a small filter, and the black precipitate is tested for Ni by fusing the portion of the filter-paper, which is stained by the NiS, into a colourless borax-bead. If the bead is *violet* or *brown* while hot and *yellow* when cold after it has been heated in the outer flame, and *becomes grey or opaque* after it has been heated in the inner flame, Ni is certainly present, and need not be further tested for in Table III.B. (1257).

The colourless filtrate, from which the $Cr(OH)_3$ or the NiS has been separated by boiling in the dish, is then examined by the General Table for Groups IV. and V.

1249. Part of the precipitate, which has been produced by Am_2CO_3, often adheres firmly to the inside of the vessel in which it has been produced. If this is the case, the tube should be rinsed out several times with distilled water, and the precipitate dissolved by pouring in some hot HĀ and causing it to run over the inside of the tube. This solution is added to the HĀ-solution of the Am_2CO_3-precipitate, which is subsequently prepared for Table IV. (1261).

Since the precipitation with Am_2CO_3 is often somewhat slow, it is advisable to allow the warm solution to stand for a few minutes before filtering or passing on. If only a slight turbidity is caused, it may be removed by filtration and examined for the metals of Group IV., the spectroscope serving to detect mere traces of the metals in a strong solution.

1250. The precipitate produced by HCl may consist of $PbCl_2$, AgCl, and $Hg^{\cdot}_2Cl_2$: it is washed several times on the filter with boiling water, the first washings being kept apart :—

<table>
<tr>
<td rowspan="2">The first portions of the washings may contain $PbCl_2$, in solution: if this is present in any quantity, it will be deposited in brilliant colourless crystals as the liquid cools.

Test for, or confirm the presence of Pb, by adding K_2CrO_4 to the washings: a yellow precipitate, readily soluble in KOH, shows :—

Presence of Pb.</td>
<td colspan="2">Residue: the residue is rinsed into a test-tube (50, a.f.) and boiled with AmOH, and the liquid is then filtered :—</td>
</tr>
<tr>
<td>Filtrate: add HNO_3 until liquid is acid: a white precipitate, which unites into curdy particles when the liquid is shaken or boiled, shows :—

Presence of Ag.</td>
<td>Residue on the filter: dissolve in a little aqua regia, add AmOH in excess, and then HCl in excess: warm the solution and drop into it a small bright strip of Cu: a grey deposit which becomes silver-white when it is rubbed proves :—

Presence of $Hg^{\cdot}$ (Mercurosum).

[Another method of testing this residue for Hg will be found in 1253.]</td>
</tr>
</table>

TABLE G.—EXAMINATION OF THE PRECIPITATE FORMED BY BOILING THE HCl-SOLUTION WITH H_2SO_3. (See par. 1240.)

1251. This precipitate may contain Au, $PbSO_4$, $BaSO_4$, and $SrSO_4$; the last three substances are perfectly white, and if Au is present it is usually seen by colouring the precipitate brown or black; the Au is also usually visible during precipitation by H_2SO_3, or after the white sulphates have subsided, since it colours the liquid blue by transmitted and reddish by reflected light.

Ba and Sr can be tested for at once as is directed in the last part of par. 1245, by heating a little of the moist precipitate on a loop of platinum-wire in the inner blowpipe-flame, moistening with HCl, and trying the flame-coloration.

A more trustworthy method of procedure is the following :—

Rinse the precipitate into a small porcelain dish, using as little water as possible; add a few drops of strong $H\bar{A}$, or dissolve in the liquid a small crystal of H_2T, then add AmOH until it is just in excess, and boil for a few minutes; let the liquid stand for a short time, and decant through a filter :—

<table>
<tr>
<td rowspan="2">Solution: add $H\bar{A}$ in excess, then K_2CrO_4; a yellow precipitate, soluble in KOH, shows :—

Presence of Pb.</td>
<td colspan="2">Residue: pour upon the residue in the dish a little HCl and a few drops of HNO_3, heat to boiling, let stand, and decant into a porcelain dish :—</td>
</tr>
<tr>
<td>Solution: boil until the smell of Cl is removed, and add several drops of fresh $FeSO_4$-solution; a blue coloration and reddish precipitate show :—

Presence of Au.</td>
<td>Residue: dry by gently heating the dish, fuse with Na_2CO_3 on platinum-foil, and examine the mass for Ba and Sr as is directed in the last part of par. 1245.</td>
</tr>
</table>

1252. The precipitate produced by H_2S in the HCl-solution, after it boiled with a small quantity of yellow Am_2S (*Note* 1), or with much

GROUP II.A.—COPPER GROUP.

1253. *The Residue* may contain HgS, PbS, Bi_2S_3, CuS, CdS. After the precipitate has been washed and allowed to drain, remove it from the filter into a porcelain dish (50, *d*), pour upon it strong HNO_3 sufficient to cover it completely, and heat gently as long as any red fumes come off, adding more strong HNO_3 if necessary to prevent evaporation to dryness. Boil off nearly all the acid, add a little dilute H_2SO_4, let stand for some time, stirring occasionally, and filter:—

<table>
<tr>
<td colspan="2">Residue may contain HgS (black), $PbSO_4$ (white); but if white, the absence of Hg is not proved.
Remove the residue into a porcelain dish, using as little water as possible; add a little HĀ, then AmOH in excess, boil and filter:—</td>
<td colspan="3">Filtrate may contain Bi, Cu, Cd.
Add AmOH in excess, boil and filter:—</td>
</tr>
<tr>
<td rowspan="2">Residue: dry on the filter at a gentle heat, scrape the dried residue off the filter (Note 2), and heat it, mixed with dry Na_2CO_3, in a small ignition-tube; globules of Hg are seen on the inside of the tube when it is rubbed or examined by a lens:—

Presence of Hg'' (Mercuricum).

[For another method, see 1250.]</td>
<td rowspan="2">Filtrate: Add HĀ in excess, then K_2CrO_4, a yellow precipitate:—

Presence of Pb.</td>
<td rowspan="2">Precipitate (not easily seen in dark blue solutions): wash with hot water, dissolve off the filter by pouring upon it a few drops of boiling dilute HCl, and let this solution drop into a large quantity of cold distilled water: a milkiness appearing at once or after stirring and letting stand for some time, shows:—

Presence of Bi.

Note.—A precipitate produced by AmOH must always be tested as above for Bi, since Pb and Hg might possibly appear here as white precipitates and be mistaken for Bi.</td>
<td colspan="2">Filtrate may contain Cu and Cd: if blue, it contains Cu (Note 3). Add HCl until the liquid is acid, then add H_2S in excess, filter and wash quickly, keeping the filter covered with a glass plate; rinse the precipitate into a test-tube, pour upon it some dilute H_2SO_4, boil and filter through a covered filter (Note 4):—</td>
</tr>
<tr>
<td>Residue: dissolve by pouring a little boiling dilute HNO_3 upon the filter, add to the solution AmOH in excess, then HĀ in excess and a few drops of K_4FeCy_6-solution: a chocolate-red precipitate shows:—

Presence of Cu.</td>
<td>Filtrate: add much H_2S-water, or add much water and pass H_2S for some time: a yellow precipitate shows:—

Presence of Cd.

Note.—If this precipitate is dark-coloured, CuS is present (see Note 4): filter it off, boil it once more with H_2SO_4; filter rapidly and test the filtrate by H_2S for Cd.</td>
</tr>
</table>

Note 1.—If traces of Cu have to be tested for, Na_2S should be substituted for
readily soluble in Am_2S.

Note 2.—If the residue is too small to be removed, the portion of the paper con-
in performing this test refer to paragraph 140.

Note 3.—Another method of detecting Cd in the presence of Cu, consists in adding
as yellow sulphide; Cu may then be tested for in the filtrate, which has been boiled
in excess, and K_4FeCy_6 (158).

Note 4.—Unless this precipitate is filtered without delay in a covered funnel,
into the filtrate as $CuSO_4$; it then discolours the CdS precipitate, and may be
of H_2S-water into the funnel with each fresh addition of washing water.

Note 5.—*White* S will always be precipitated here, if *yellow* ammonium sulphide
of the white liquid with benzene. The coloured sulphide is seen at the surface

Note 6.—The detection of As, Sb, Sn by the method given in par. 1254 is simple and
graphs 206 and 207; but these methods need not be resorted to unless Au or Pt,

Note 7.—The Pt-foil is removed and washed, and the Sb-deposit is dissolved by
is cooled and mixed with H_2S-water, or diluted and saturated with H_2S, an orange-
hours, confirming the *Presence of Sb*.

Note 8.—The addition of H_2S to the HCl-solution in the General Table (1235)
[illegible]tion occurring only on the application of heat, whether As and Sn were originally
203 must be tried on the [illegible] solution of the substance.

ıas been washed with hot water, is removed from the filter (50, *d*) and
ΚOH-solution, and filtered :—

GROUP II.B.—ARSENIC GROUP.

The Filtrate may contain As_2S_3, Sb_2S_3, SnS_2, SnS, [Au_2S_3, PtS_2], combined with alkaline sulphide. Add to it HCl until it is acid, and pass H_2S unless the liquid smells strongly; the above sulphides, if present, will be reprecipitated; a mere milkiness due to precipitation of S may be disregarded. (*Note* 5.) The precipitate is filtered off and examined as is directed below (1254). See *Note* 6.

1254. *The Precipitate* is allowed to drain for some time upon the filter in the funnel, and is further freed from water by carefully taking the filter out of the funnel, opening it out, and spreading it upon a pile of three or four filter-papers. The precipitate is then removed to a small porcelain dish (50, *d, f*) and heated for some time nearly to boiling with strong fuming HCl: the liquid is then cooled and filtered :—

The Residue will consist of As_2S_3, which is almost insoluble in strong HCl.

Dry the washed residue on the filter at a gentle heat, then mix it with three or four times as much powdered KCN and freshly-dried Na_2CO_3, and heat the mixture in a small bulb-tube, removing any drops of water inside the tube by a twisted piece of filter-paper; a black mirror (181) :—

Presence of As.
(Refer to *Note* 8.)

Note.—The As_2S_3 may also be dissolved by heating it with a little fuming HNO_3: the excess of HNO_3 is then boiled off and As is detected as H_3AsO_4 by adding AmCl, excess of AmOH and $MgSO_4$ (186); or by addition of $AgNO_3$, and then cautiously neutralising with AmOH (184).

The Filtrate may be examined for Sb and Sn by either I. or II. below :—

I. Place a piece of platinum-foil in a porcelain dish and pour the acid filtrate upon it, then drop upon the foil a piece of Zn; H will come off with effervescence, and if either at once or after a few minutes a black stain appears upon the platinum the *Presence of Sb* is indicated. Confirm as is directed in *Note* 7.

Remove the platinum-foil and drop in pieces of Zn: as soon as the bubbles of H cease to be given off, Zn still remaining undissolved, remove the pieces of Zn, rubbing and rinsing any dark deposit back into the dish (199); let this deposit settle, decant the liquid and heat the solid deposit with strong HCl for several minutes in a test-tube, dilute with a little water, filter if necessary, and add a few drops of $HgCl_2$-solution: a white or grey precipitate (202) indicates :—*Presence of Sn* (*Note* 8).

[Refer to 1304, 1305, if Au and Pt have to be tested for.]

II. The acid filtrate is poured into a little hydrogen-flask (Fig. 51, page 82), in which H has been coming off briskly for about five minutes, being produced by the action of a little dilute HCl upon some stick Zn. The H is lighted at the jet, and the inside of a small porcelain dish or crucible lid is pressed down upon the flame: a black stain which is not dissolved by solution of bleaching-powder shows :—*Presence of Sb.*

The residue in the flask is tested for Sn, as is directed in the latter part of I. (above).

Am_2S, since CuS is somewhat soluble in Am_2S; but SnS and Au_2S_3 are much more

taining it may be cut up and mixed with the Na_2CO_3. For the precautions requisite

KCN-solution to the blue ammoniacal liquid, and passing H_2S; Cd if present falls
down considerably with excess of HNO_3, by adding AmOH in excess, then HA

washed quickly, and examined at once, CuS is liable to be oxidised and to pass
entirely overlooked if present in small quantity. It is well to pour a few drops

has been used above. Traces of the sulphides are detected by shaking up a part
of contact of the benzene with the acid liquid.
rapid. It is excelled in delicacy and trustworthiness by the methods given in para-
or traces of As, Sb, Sn have to be tested for.
heating the foil in a test-tube with a little very dilute HNO_3. When this solution
red precipitate will form either at once or after the liquid has stood for some

may have already indicated by the colour of the sulphide precipitate, or by the pre-
present in the *-ous* or *-ic* condition. If this is not certain, tests 184–186 and 201–

TABLE III.A.—IRON GROUP.

1255. The precipitate produced by boiling, after the addition of AmCl and of AmOH in excess, may contain $Al(OH)_3$, $Cr(OH)_3$, $Fe(OH)_3$: the colour of the precipitate will usually show whether it contains any quantity of $Fe(OH)_3$ (reddish-brown), or $Cr(OH)_3$ (pale green), since $Al(OH)_3$ is colourless. The precipitate may be examined by I. or by II., below.

I. Dissolve the precipitate in a *little* boiling dilute HCl (50, *d, e, f*), add to the solution pure KOH- or NaOH-solution until the precipitate remains after the liquid has been stirred, then add more KOH or NaOH, boil for some time and filter :—

<table>
<tr>
<td rowspan="2">1. Filtrate may contain $Al(OH)_3$ dissolved in excess of NaOH.
If it is green, $Cr(OH)_3$ is also in solution and must be precipitated by further boiling in a porcelain dish, and then be removed by filtration.
Add HCl in slight excess, then AmOH in slight excess: a colourless gelatinous precipitate shows :—

Presence of Al.

Note.—NaOH and KOH may contain some $Al(OH)_3$: the analyst must ascertain that the Al does not come from this source.</td>
<td colspan="2">2. Precipitate may contain $Cr(OH)_3$ and $Fe(OH)_3$.
Dry upon the filter, and carefully avoid charring the paper; when sufficiently dried the substance will have shrunk considerably into small, hard, dark-coloured pieces; detach these from the filter and heat them with a little fused Na_2CO_3 and KNO_3 upon a piece of platinum-foil. Continue the fusion by heating the under surface of the foil in the blowpipe-flame as long as any frothing occurs, then allow to cool; a yellow mass indicates the presence of Cr (Note 1). Boil the platinum-foil in a small porcelain dish with water until the substance is entirely dissolved, or only a dark brown powder (Fe_2O_3) remains undissolved; take out the foil, allow the powder to settle, and decant the liquid through a filter :—</td>
</tr>
<tr>
<td>3. Filtrate will be yellow if Cr is present (Note 2).
Add $H\bar{A}$ in excess, shown by the colour becoming reddish, boil for several minutes, then add $Pb\bar{A}_2$-solution; a yellow precipitate shows :—

Presence of Cr (Note 3).</td>
<td>4. Residue in porcelain dish; dissolve by pouring in a little HCl and boiling, add some water, then a few drops of KCNS-solution; a blood-red coloration shows :—

Presence of Fe (Note 4).</td>
</tr>
</table>

II. An alternative method consists in adding Na_2O_2, little by little, to the above HCl-solution of the group-precipitate, until the liquid is strongly alkaline: or NaOH may be first added in excess followed by H_2O_2 in excess. The liquid is then boiled until effervescence ceases, and is filtered. The filtrate will contain Na_2CrO_4 and $NaAlO_2$. If Cr is present the solution will be yellow, and part of it may be tested for Cr as is described in column 3 above. The Al may be detected in another portion of the filtrate by column 1 above. If Fe is present the residue will be brown $Fe(OH)_3$, treat this as is directed in column 4 above.

Note 1.—Mn is often precipitated with the Fe, and imparts to the fused mass a bluish-green colour. The presence of Mn should be noted here, as it may be entirely precipitated in this Group, and not detected in Group III.B.

Note 2.—The green colour, caused by Mn, conceals the yellow colour due to Cr. But when the cool mass is dissolved in water and the solution is boiled with $H\bar{A}$, the manganese coloration is destroyed, and the yellow colour becomes evident after any brown manganic hydroxide has been removed by filtration.

Note 3.—Cr may have been originally present as a chromic salt or as a

chromate. Ascertain in what state Cr was present, by boiling some of the original substance with Na_2CO_3-solution and filtering. A yellow filtrate, which, after it has been acidified with $H\bar{A}$, gives a yellow precipitate with $Pb\bar{A}_2$-solution, shows that Cr was *Present as a Chromate.* If the Cr was present as a chromic salt, it will not colour the filtrate yellow.

Note 4.—Fe is always detected here as a ferric salt, since the solution has been boiled with HNO_3, in the General Table. In order to ascertain in which condition Fe was originally present, some of the substance under analysis is boiled with HCl in a special apparatus (Figs. 40, 41, page 21), the solution is filtered, if necessary, and is then divided into two parts. To one portion freshly-made solution of K_3FeCy_6 (*Note*, 279) is added, a dark blue precipitate shows the *Presence of* $Fe^{\cdot\cdot}$ (*Ferrosum*) ; to another portion KCNS is added, a blood-red colour shows the *Presence of* $Fe^{\cdot\cdot\cdot}$ (*Ferricum*).

TABLE III.P.—PHOSPHATE GROUP.

1256. If $(PO_4)'''$ has been found in the General Table by the molybdate test in a small portion of the filtrate from Group II., and a precipitate has been formed by adding to the rest of the solution AmCl and AmOH, the AmOH must be added in slight excess, and HCl must then be added with constant stirring to the turbid liquid, in quantity just sufficient to redissolve the precipitate.

A little $H\bar{A}$ is then added and some saturated $Am\bar{A}$-solution :—

a. If a precipitate forms, add $FeCl_3$-solution drop by drop with constant stirring until the liquid remains red in colour.

b. If $Am\bar{A}$ causes no distinct precipitate, add a little Am_2HPO_4-solution, and then $FeCl_3$-solution gradually until the liquid is just reddened (*Note*).

Now boil the turbid liquid in a flask or dish for a few minutes, and filter at once :—

<table>
<tr><td colspan="2">1. The Precipitate is rejected if $FeCl_3$ has produced a precipitate after $Am\bar{A}$ has failed to do so (a).
If this was not the case (b), dry the precipitate on the filter, and heat it with a fused mixture of Na_2CO_3 and KNO_3 on platinum-foil, boil the cool mass with water and filter :—</td><td rowspan="2">2. Filtrate should be free from (PO_4) and should give no precipitate with AmCl and AmOH.

Proceed to examine this for Groups III.B., IV. and V. by the procedure in the General Table (1235), and begin by adding Am_2S to precipitate Group III.B.</td></tr>
<tr><td>Residue of Fe_2O_3 may be rejected.

Test the HCl-solution of the original substance for $Fe^{\cdot\cdot}$ and $Fe^{\cdot\cdot\cdot}$ as is directed in Note 4 (1255).</td><td>Filtrate, if yellow, contains Cr : acidify a portion with $H\bar{A}$ and add $Pb\bar{A}_2$-solution ; a yellow precipitate confirms:—

Presence of Cr.

Add to the rest of the filtrate much AmCl-solution : a colourless gelatinous precipitate shows :—

Presence of Al.</td></tr>
</table>

Note.—An explanation of the principles upon which this Table depends will be found in paragraphs 1292, 1293.

TABLE III.B.—ZINC GROUP.

1257. The precipitate produced by Am_2S in the solution, or in the filtrate from Group III.A., may contain ZnS, MnS, NiS, CoS. The colour of the precipitate will usually show whether it contains any quantity of NiS or CoS which are black, or consists only of MnS (pink), or of ZnS (white).

The presence of Ni will have been indicated in the General Table (1235) by the blue colour of the filtrate which was obtained after boiling with AmOH, and by the dark brown colour of the filtrate which was obtained after boiling with yellow Am_2S. If the black precipitate, which was obtained by boiling the dark brown filtrate from Am_2S (1248), has been proved by the borax-bead to be NiS, the further tests for Ni in the following Table may be omitted.

Remove the precipitate from the filter with cold dilute HCl in the way described in par. 50, *c*; take out the paper and allow the liquid to stand, occasionally stirring it well. The precipitate will either dissolve leaving only white sulphur, and the milky liquid may be at once examined by 1259; or a black residue will be left, which must be filtered off and examined by Table 1258, the filtrate being examined by Table 1259.

1258. *The Residue* is black, and may contain NiS, CoS: examine it by I. and II. below:—

I. *Examination by the Borax bead.* Fuse a small quantity of the residue in a clear borax bead in the extreme tip of the outer blowpipe-flame, and note its colour; then fuse the bead for some time in the inner blowpipe-flame, and again observe its colour:—

Blue bead in both flames shows:— *Presence of Co.* Co need not be further tested for, but if any doubt exists as to the presence of Ni the rest of the residue must be examined as below.	*Brown or yellow bead,* when cold after fusing it in the outer flame, which becomes *grey or opaque* in the inner flame, shows *Presence of Ni, Absence of Co.* Unless a trace of Co has to be tested for, no further examination need be made.	*A bead which is neither brown nor blue,* but of some intermediate hue on cooling from the outer flame, indicates the probable presence of both Co and Ni. Examine the remainder of the black residue as is directed below for Ni and Co, or for Co alone if Ni has been already detected by par. 1248.

II. *Further Examination of the Residue.*—Rinse the residue from the filter into a porcelain dish, using as little water as possible: pour in a little strong HCl and boil for some time adding occasionally a small crystal of $KClO_3$, until the black residue is entirely dissolved or only a small quantity of dark sulphur remains; then boil down nearly to dryness [a blue liquid shows *Presence of Co*], dilute with a little water, filter if necessary into a boiling-tube and pour in KCN-solution slowly until any visible precipitate disappears, or until the liquid is alkaline, boil briskly for several minutes, and add much strong NaOCl-solution; or make decidedly alkaline with NaOH and add much Br-water; heat nearly to boiling, allow the liquid to stand at least ten minutes, and filter. [Any black film on the inside of the tube is dissolved in boiling HCl, precipitated by NaOH-solution and added to the precipitate below]:—

Precipitate (black): wash, and confirm the presence of Ni by fusing some of the precipitate, or the paper stained with the precipitate, in a borax bead, first in the outer, then in the inner blowpipe-flame: a bead *yellow* when cold, becoming *black* in the inner flame shows:— *Presence of Ni.*	*Filtrate* must be warmed with more NaOCl, or Br-water, and filtered from any additional precipitate which may form, then evaporated to dryness, and strong HNO_3 poured upon the residue as long as any frothing is caused; this is then evaporated just to dryness, the residue dissolved in water, excess of KOH added to it, and any precipitate filtered off, and this, or the paper stained by it, is fused into a borax bead: a blue bead shows:— *Presence of Co.*

1259. *The Solution or Filtrate* may contain Zn, Mn. Boil it in a porcelain dish until it ceases to smell of H_2S, then drop in a small crystal of $KClO_3$, and boil for several minutes. After cooling add pure NaOH-solution, until after stirring the liquid it turns red litmus-paper blue, then add more NaOH-solution, stir well and filter :—	
Precipitate is white at first, but rapidly darkens in the air. Heat a portion of it with fused Na_2CO_3 and KNO_3 on platinum-foil ; a bluish-green mass is obtained on cooling, showing :— *Presence of Mn.* *Note.*—Mn may have been originally present either in the basic or acidic form. Its presence in acidic form is indicated by the colour of the original solution, since in the form of manganate it is green, and as permanganate it is purple ; and these colours will have disappeared on boiling the HCl-solution for some time, or on adding H_2S.	*Filtrate* ; pass H_2S, a white precipitate forms, often somewhat discoloured, showing :— *Presence of Zn.* *Note.*—From a dilute solution of $Zn(OH)_2$ in NaOH the $Zn(OH)_2$ is precipitated by boiling ; hence after adding NaOH, as is directed above, the liquid must not be boiled, else Zn might be precipitated with the $Mn(OH)_2$ and escape detection. But by diluting and boiling the above filtrate, it is usually possible to cause any $Zn(OH)_2$ which it holds in solution to precipitate, especially if the alkalinity of the liquid has been somewhat reduced by the cautious addition of HCl in quantity insufficient to make the liquid acid. If this precipitate is separated by pouring the liquid through a double filter, and is then dissolved off the filter and the sides of the boiling tube by a little boiling HĀ, ZnS may be precipitated *perfectly white* from this solution by the action of H_2S.

TABLES IV AND IV.A.—BARIUM GROUP.

1260. The precipitate, which has been produced by Am_2CO_3 and may contain $BaCO_3$, $SrCO_3$, $CaCO_3$, is first examined by flame-coloration, and the results thus obtained may afterwards be confirmed by the wet method, as is directed in par. 1261, or by the quicker method in par. 1262.

Examination by Flame-coloration.—Take a small quantity of the precipitate off the filter upon the end of a glass rod, and dissolve it by moving the end of the rod about in several drops of HCl on a watch-glass ; dip into this solution a loop of platinum-wire, which imparts no colour to the flame (62, Exp. 31), and hold the loop for some time in the Bunsen-flame.

Ca will impart to the flame a *yellowish-red* colour, Sr a *crimson-red*, Ba a *yellowish-green*. The red colorations yielded by Ca and Sr are distinguished by viewing the flame through the indigo-prism ; the Ca coloration then appears *dingy green*, while the Sr-coloration still appears *crimson*. Ba is usually found by its coloration remaining after the other colorations have disappeared. When all three metals are present together, their colorations are apt to interfere with one another ; but if at any time a red colour is visible through the indigo-prism, Sr is certainly present ; if a green coloration is visible without using the prism, the presence of Ba is proved. The flame-coloration should also be examined by the spectroscope (63).

1261. *Examination in the Wet Way.*—Dissolve the rest of the precipitate off the filter by pouring in a little boiling HĀ, and boil the liquid and pour it again through the filter if the precipitate is not entirely dissolved. If the solution is not acid in reaction, mix more HĀ with it, then pour off a small portion (*A*) of the solution into a test-tube, and put by the larger portion (*B*). Cool portion

BARIUM GROUP

These lines run across both pages.

<table>
<tr><td colspan="3">I. An immediate precipitate is produced by $CaSO_4$ in the cold, showing :—
Presence of Ba.
Portion (B) must then be tested for Sr and Ca which may also be present: examine it as is directed below :—
Add K_2CrO_4-solution until the colour of the liquid is reddish-yellow, heat, and filter through a double filter-paper, pouring the filtrate through the same filter repeatedly, if necessary, until the liquid is quite clear; then add to the liquid, which must be orange-red in colour indicating excess of HĀ and of chromate, AmOH until the colour changes to pale yellow, then add Am_2CO_3-solution :—</td></tr>
<tr><td rowspan="2">No precipitate forms, showing :—
Absence of Sr and Ca.</td><td colspan="2">A precipitate forms, showing Sr, Ca, or both of them, to be present. Add to the liquid Am_2CO_3 in excess, filter, reject the filtrate and dissolve the precipitate off the filter in as little boiling HĀ as possible; pour off a small part (C) of this solution, reserving the larger portion (D). To (C) add $CaSO_4$-solution and boil :—</td></tr>
<tr><td>A precipitate forms :—
Presence of Sr.
Examine portion (D) for Ca as is directed at (D), Column II.</td><td>No precipitate forms :—
Absence of Sr.
Examine portion (D) for Ca as is directed at (D) in Column III.</td></tr>
</table>

(*A*) and add to it several drops of $CaSO_4$-solution; if an immediate precipitate forms, refer to column I. below, or to IV. (1262): if no immediate precipitate forms heat the liquid to boiling, and if a precipitate then forms refer to II. below, or to V. (1262); if no precipitate forms even after several minutes, test portion (*B*) by III. below, or by VI. (1262).

—TABLE IV.

II. *A precipitate is not formed at once on the addition of $CaSO_4$, but appears on boiling the liquid, showing :—*	III. *No precipitate is produced by $CaSO_4$, even on boiling, showing :—*
Absence of Ba and Presence of Sr.	*Absence of Ba and Sr, and Presence of Ca.*
D. Portion (*B*) is then examined for Ca as directed below :— Add dilute H_2SO_4, boil, filter, and reject the precipitate; add to the filtrate several drops of H_2SO_4 and boil; if this causes any precipitate, boil and filter, and again test the filtrate by addition of H_2SO_4 and boiling: repeat this process if necessary. To the clear filtrate, which gives no further precipitate on the addition of H_2SO_4 and boiling, add gradually AmOH until after mixing the liquid by thorough stirring or shaking, it turns red litmus-paper blue, then add $Am_2C_2O_4$-solution and warm gently; a white precipitate, often appearing only after a time, shows :—	*D.* Confirm the presence of Ca by making portion (*B*) alkaline with AmOH, and then adding $Am_2C_2O_4$-solution; a white precipitate forms, showing :—
Presence of Ca.	*Presence of Ca.*

—TABLE IV.A.

V. *In the Solution or Filtrate* test for Sr, Ca.	VI. *The Solution or Filtrate* may contain Ca.
Dilute with water; then add dilute H_2SO_4, boil and filter, repeating the process until no further precipitate is produced. *The Precipitate*: moisten with strong HCl, and test for Sr by the flame-coloration, using the indigo-prism, or the spectroscope (411). *The Filtrate* is examined by Column VI.	Add AmOH in excess, then add $Am_2C_2O_4$ and allow to stand: a white precipitate shows the :— *Presence of Ca.*

TABLE V.—POTASSIUM GROUP.

1263. The filtrate, which remains after all the Group-reagents have been added in succession to the original solution, may still contain Mg, K, Na, Li and NH_4.

Since, however, NH_4-salts have been added as Group-reagents, NH_4 must be tested for in the original substance by KOH-solution (1218, I, 3).

Proceed to examine for other members of Group V. as is directed below.

Evaporate the filtrate from Group IV. to dryness in a porcelain dish, scrape out the solid residue, and heat it to redness upon a piece of platinum-foil in the Bunsen-flame as long as any white fumes are seen to be given off when the foil is removed for an instant from the flame (*Note* 1). All NH_4-compounds are thus entirely removed.

Dissolve any residue which remains (*Notes* 2, 3), by boiling the foil in a test-tube with a small quantity of water, to which several drops of dilute HCl have been added, and divide this solution into two parts :—

<table>
<tr><th>I. EXAMINATION FOR Mg.</th><th colspan="2">II. EXAMINATION FOR K, Na AND Li.</th></tr>
<tr><td rowspan="3">Before testing for Mg in one portion of this solution, it is necessary to remove from it any traces of Ba, Sr, or Ca which it may possibly contain, and which might else be mistaken for Mg.

Add, therefore, several drops of H_2SO_4 to the liquid, boil for a short time and then, whether a precipitate has formed or not, add a little AmCl, then AmOH in excess, then several drops of $Am_2C_2O_4$; if any precipitate forms, filter and add to the filtrate Na_2HPO_4, and if no precipitate forms at once, let the liquid stand for some time: a white crystalline precipitate shows :—

Presence of Mg.</td><td colspan="2">In the other portion test for K and Na as is directed below, referring to Note 3 if Li may be present.
Flame coloration.—Dip into the solution a loop of platinum-wire, which has been proved not to impart any colour to the flame, and hold the loop in the Bunsen-flame; one of the following results will be observed :—</td></tr>
<tr><td>A bright yellow flame coloration, indicating the presence of Na (Note 4).
Examine this coloration through the indigo-prism; if it appears red, Presence of K is probable (443, and Note 3): if no red colour is visible K is probably absent, or is present only in very minute quantity.</td><td>A pale lilac coloration, appearing crimson red through the indigo-prism, shows :—

Presence of K, and absence of Na.</td></tr>
<tr><td colspan="2">It is usual to confirm the results of the examination of the flame coloration by pouring the remainder of the solution upon a watch-glass, adding to it several drops of H_2PtCl_6-solution (420, Note), (See Note 5), or a little sodium picrate solution, and stirring well for some time; the formation of a yellow precipitate shows :—

Presence of K.

See par. 421, and Note 6 below.</td></tr>
</table>

Note 1.—If the residue is small in amount, it may be ignited in the dish; but this is not to be generally recommended, since the porcelain dish is liable to be cracked by the heat, and it is also difficult to get entirely rid of the NH_4-salts by heating the residue in porcelain.

Note 2.—It is not safe to place much reliance upon an examination of the

foil for the detection of a small quantity of the transparent residue, but it may usually be detected by producing a crackling noise while the foil is cooling immediately after its removal from the flame. Should there be any doubt, the foil must be boiled with water and a drop of dilute HCl, and the solution examined for Mg, K, and Na, as is directed in the above Table.

If Li is to be separated and detected refer to *Note* 3.

Note 3.—If Li may be present and is to be tested for, the above residue (*Note* 2) must be treated in such a way as to convert the metals into chlorides.

It is dissolved in a little water and $BaCl_2$-solution is added drop by drop as long as it produces any precipitate: then $Ba(OH)_2$-water is added until the liquid is strongly alkaline to test-paper: the liquid is then boiled and filtered: the filtrate is made just acid with dilute HCl, and the Ba is completely removed by adding AmOH and Am_2CO_3 in excess and filtering. The filtrate is evaporated to dryness, and the residue freed from Am-salts by ignition on Pt-foil. The residue is once more dissolved in a little water, and mixed with Am_2CO_3-solution, and any precipitate of $BaCO_3$ is filtered off. The clear liquid is once more evaporated to dryness, and the residue is ignited to free it from Am-salts.

The residue, in which only chlorides are present, is now extracted with a mixture of absolute alcohol and ether: the residue left on evaporation of this extract is dissolved in a few drops of dilute HCl, and this solution will give the red flame-coloration and spectrum-band of Li (443).

The residue left undissolved by the ether and alcohol is then dissolved in a little water and a drop of dilute HCl, and tested for Mg, K and Na. It must be remembered that Li cannot be distinguished from K by examining their flame-coloration through the indigo-prism, but only by the spectroscope (443).

Note 4.—The examination of this flame-coloration by means of the spectroscope (63) should be made if possible.

A yellow flame coloration, more or less intense, will almost always be obtained here, since most substances and reagents contain small quantities of Na. Hence the student must note the intensity of the coloration, and judge from it whether the quantity of Na is small or large. The test for a trace of Na is usually made upon the original substance (1219).

Note 5.—If iodine is present, H_2PtCl_6 will produce an intense red coloration. Hence if iodine is suspected to be present, the above solution should be evaporated to dryness with a little strong HNO_3, and the residue dissolved in a few drops of dilute HCl before it is tested for K with H_2PtCl_6.

This is of course unnecessary, if the solution has already been evaporated to dryness with HNO_3 before precipitating Group III. in the General Table. In case of uncertainty, add H_2PtCl_6 to a drop only of the above solution, and if iodine is found to be present proceed as is directed above.

Note 6.—Mere traces of K and Na may be detected by adding H_2PtCl_6 and evaporating the liquid to dryness in a porcelain dish upon a water-bath. Absolute alcohol is then poured into the dish and stirred. Any yellow residue shows the *Presence of K.*

The solution will give the pure Na-coloration, if Na is present: and if the yellow residue is filtered off and washed with absolute alcohol, it will yield the pure lilac flame-coloration of K.

EXAMINATION FOR ACID-RADICLES

1264. In conducting the Examination for Acid-radicles, much time and trouble may usually be saved by considering which of these radicles can possibly be present. Their number may usually be considerably reduced by a reference to the Table of Solubility (1266), since the analyst knows at this stage both the solubility of the substance and also what metals it contains. The number of acid-radicles to be tested for may then usually be further reduced, by a consideration of what radicles have been proved to be present or absent by the preceding Examinations (1267).

1265. **The following Table of Solubility** only includes the commonly occurring compounds of the more abundant metals. The solubility of other substances may be obtained by reference to special books.

The Table is thus arranged. In a horizontal line at the head are

1266. SOLUBILITY OF THE OXIDES

	Acetate	Arsenate	Arsenite	Borate	Bromide	Carbonate	Chlorate	Chloride	Chromate	Cyanide	Ferricyanide	Ferrocyanide	Fluoride	Hypophosphite
Silver	W.[3]	D.N.	D.N.	D.N.	i.	D.N.	W.[3]	i.	D.N.	C.N.	i.	i.	W.	—
Mercurous	W.	D.N.	D.N.	D.N.	C.N.	D.N.	—	C.N.	D.N.	—	C.N.	C.N.	D.N.	—
Lead	W.	D.N.	D.N.	D.N.	W.[3]	D.N.	W.	W.[3]	D.N.	D.N.	W.[3]	D.N.	D.N.	W.[3]
Mercuric	W.	D.H.	D.H.	D.H.	W.[3]	D.H.	W.	W.	D.H.	W.	W.	D.H.	D.N.	—
Bismuth	W.	D.H.	—	D.H.	D.H.[5]	D.H.	—	D.H.[5]	D.H.	D.H.[5]	D.H.	D.H.	D.H.	—
Cuprous	—	—	—	—	C.H.	—	—	C.H.	—	C.N.	—	—	C.H.	—
Cupric	W.	D.H.	D.H.	D.H.	W.	D.H.	W.	W.	D.H.	D.H.[5]	i.	i.	D.H.	W.
Cadmium	W.	D.H.	—	D.H.	W.	D.H.	W.	W.	D.H.	W.[3]	C.H.	C.H.	W.[3]	W.
Stannous	W.[5]	D.H.	D.H.	D.H.	W.[5]	—	—	W.[5]	—	—	C.H.	C.H.	W.	—
Stannic	—	C.H.	—	—	W.[5]	—	—	W.[5]	—	—	—	—	W.	—
Arsenious	—	—	—	—	—	—	—	W.	—	—	—	—	—	—
Antimonious	—	—	—	—	D.H.	—	—	D.H.	—	—	—	—	W.	—
Antimonic	—	—	—	—	—	—	—	W.[5]	—	—	—	—	W.	—
Aluminium	W.	D.H.	—	D.H.	W.[5]	—	W.	W.[5]	D.H.	—	W.	W.[3]	W.	W.
Chromic	W.	D.H.	W.	D.H.	W.[6]	—	W.	W.[6]	—	—	W.	W.	D.H.	W.
Ferrous	W.	D.H.	D.H.	D.H.	W.	D.H.	—	W.	D.H.	—	C.H.	C.H.	W.[3]	W.
Ferric	W.	D.H.	D.H.	D.H.	W.[5]	—	W.	W.[5]	D.H.	—	W.	C.H.	W.[3]	W.[3]
Zinc	W.	D.H.	D.H.	D.H.	W.[5]	D.H.	W.	W.[5]	D.H.	D.H.	D.H.	C.H.	W.[3]	W.
Manganese	W.	D.H.	D.H.	D.H.	W.	D.H.	—	W.	D.H.	—	D.H.	D.H.	D.H.	W.
Cobalt	W.	D.H.	D.H.	D.H.	W.	D.H.	W.	W.	D.H.	D.H.	i.	i.	W.[3]	W.
Nickel	W.	D.H.	D.H.	D.H.	W.	D.H.	W.	W.	D.H.	D.H.	i.	C.H.	D.H.	W.
Calcium	W.	D.H.	D.H.	D.H.	W.	D.H.	W.	W.	W.	W.	W.	W.	i.	W.
Strontium	W.	D.H.	D.H.	D.H.	W.	D.H.	W.	W.	W.[3]	W.	W.	W.	D.H.	W.
Barium	W.	D.H.	D.H.	D.H.	W.	D.H.	W.	W.	D.H.	W.[3]	W.	W.[3]	D.H.	W.
Magnesium	W.	D.H.	D.H.	D.H.	W.[5]	D.H.	W.	W.[5]	W.	W.	W.	W.	D.H.	W.
Sodium	W.	W.	W.	W.	W.	W.	W.	W.	W.	W.	W.	W.	W.	W.
Potassium	W.	W.	W.	W.	W.	W.	W.	W.	W.	W.	W.	W.	W.	W.
Ammonium	W.	W.	W.	W.	W.	W.	W.	W.	W.	W.	W.	W.	W.	W.

W. = water. D.H. = dilute hydrochloric acid. C.H. = concentrated hydrochloric acid.

1 Sb_2O_4 and Sb_2O_5 are only slowly attacked by concentrated HCl.
2 The solubility in HCl of the oxides Al_2O_3, Cr_2O_3, Fe_2O_3 depends on their degree of hydration: after ignition they are almost or quite insoluble in acids.

placed the names of the more commonly occurring acid-radicles and of oxygen in alphabetical order. In the vertical column on the left and right is a list of the metals in the order of the Analytical Groups.

The Solubility of a Compound is found by following the horizontal line of the name of metal, until the vertical line headed by the acid-radicle is reached: the solubility of the compound will be indicated by the letter or letters standing at this point. The signification of these letters is explained at the foot of the Table where also will be found further information concerning certain compounds in numbered notes. It should be understood that the solubility indicated in the Table is that first arrived at by applying the solvents successively in the order stated in par. 1229, and that this would generally imply solubility also in the succeeding solvents there used. The letter which indicates the solubility of the compound will be found in a horizontal line with the acid-radicle portion of the name of the compound.

AND SALTS OF THE METALS.

Iodide	Nitrate	Nitrite	Oxalate	Oxide	Phosphate	Phosphite	Silicate	Sulphate	Sulphide	Sulphite	Thiocyanate Sulphocyanide	Tartrate	Thiosulphate	
i.	W.	W.3	D.N.	D.N.	D.N.	—	D.N.8	W.3	D.N.8	D.N.	C.N.	D.N.	W.3	Silver
C.N.	W.5	—	D.N.	D.N.	D.N.	—	—	D.N.	—	—	A.R.	D.N.	—	Mercurous
W.3	W.	W.	D.N.	D.N.	D.N.	D.N.	i.	D.N. : i.	D.N.	D.N.	C.N.	D.N.	W.3	Lead
C.N.	W.5	—	D.H.	D.H.	D.H.	—	—	D.H.5	A.R.	D.H.	D.H.	D.H.	—	Mercuric
D.H.5	D.H.5	—	D.H.	C.H.	D.H.	D.H.	D.H.8	W.5	D.N.	D.H.	D.H.	D.H.	—	Bismuth
C.H.	—	—	—	C.H.	—	—	—	—	C.N.	C.H.	C.H.	—	C.H.	Cuprous
—	W.	W.	D.H.	D.H.	D.H.	D.H.	D.H.8	W.	D.N.	D.H.	C.H.	D.H.	—	Cupric
W.	W.	W.	D.H.	D.H.	D.H.	D.H.	D.H.8	W.	D.N.	D.H.	W.3	D.H.	W.	Cadmium
W.5	—	—	D.H.	D.H.	D.H.	D.H.	—	W.5	C.H.	—	W.	D.H.	—	Stannous
D.H.	—	—	—	i.	C.H.	—	—	—	C.H.	—	—	—	—	Stannic
—	—	—	—	D.H.	—	—	—	—	C.N.	—	—	—	—	Arsenious
D.H.	—	—	D.H.	D.H.	—	—	—	—	C.H.	—	—	D.H.	—	Antimonious
—	—	—	—	C.H.1	—	—	—	—	C.H.	—	—	—	—	Antimonic
W.5	W.	—	D.H.	D.H.2	D.H.	D.H.	D.H. : i.	W.	—	—	—	W.	—	Aluminium
—	W.	—	D.H.	D.H.2	D.H.	D.H.	—	W.6	—	D.H.	W.	W.	—	Chromic
W.	W.	—	D.H.	D.H.	D.H.	D.H.	D.H.8	W.	D.H.	D.H.	W.	D.H.	W.	Ferrous
—	W.	—	D.H.	D.H.2	D.H.	D.H.	D.H.8	W.5	—	D.H.	W.	W.	—	Ferric
W.5	W.	W.	D.H.	D.H.	D.H.	D.H.	D.H.8	W.	D.H.	D.H.	W.3	D.H.	—	Zinc
W.	W.	W.	D.H.	D.H.	D.H.	D.H.	D.H.8	W.	D.H.	D.H.	W.	D.H.	W.	Manganese
W.	W.	—	D.H.	D.H.	D.H.	D.H.	D.H.8	W.	C.N.	D.H.	W.	D.H.	W.	Cobalt
W.	W.	W.	D.H.	D.H.	D.H.	D.H.	D.H.8	W.	C.N.	D.H.	W.	D.H.	W.	Nickel
W.	W.	W.	D.H.	W. : D.H.	D.H.	D.H.	D.H.	W. : C.H.	D.H.	D.H.	W.	D.H.	W.	Calcium
W.	W.	W.	D.H.	W. : D.H.	D.H.	D.H.	D.H.8	i.	D.H.	D.H.	W.	D.H.	W.	Strontium
W.	W.	W.	D.H.	W.	D.H.	D.H.	D.H.	i.	D.H.	D.H.	W.	D.H.	W.3	Barium
W.	W.	W.	D.H.	D.H.	D.H.	D.H.	D.H.8	W.	D.H.	D.H.	W.	D.H.	W.	Magnesium
W.	W.	W.	W.	W.	W.	W.	W.	W.	W.	W.	W.	W.	W.	Sodium
W.	W.	W.	W.	W.	W.	W.	W.	W.	W.	W.	W.	W.	W.	Potassium
W.	W.	W.	W.	W.	W.	W.	W.	W.	W.	W.	W.	W.	W.	Ammonium

D.N = dilute nitric acid. C.N. = concentrated nitric acid. A.R. = aqua regia. i = insoluble in acids.

6 Anhydrous chromic halides and sulphate are insoluble in acids.

7 These solubilities apply to the freshly precipitated salts. Ferro- and ferricyanides, which are insoluble in acids, are readily decomposed by alkalis.

8 Artificial silicates, which have not been strongly ignited, are decomposed by dilute HCl, gelatinous silica separating if the solution is concentrated. Some natural silicates, which are hydrated, are decomposed by strong HCl, but many silicates are unacted on by acids.

The Way in which this Table is used may be illustrated by an example. In order to ascertain the solubility of zinc sulphate, it is only necessary to glance down the vertical column with *sulphate* at its head, and on the horizontal line with *zinc* stands the letter w; this indicates that zinc sulphate is soluble in water, and would therefore have been dissolved for analysis by the first solvent used (1229): but no information is given or is required as to its solubility in the other solvents.

The Application of the Knowledge furnished by the Table may be illustrated by the following example.

In a substance, *which was entirely soluble in water*, the metals K, Ba, Ag were found. A glance along the horizontal lines opposite the names of these metals shows at once which acid-radicles may be present.

All acid-radicles might be present combined with K, since all its salts are soluble in water. But the presence of Ba, in a substance which is soluble in water, shows that the acid-radicles (SO_4), (PO_4), (CO_3), (BO_3), (AsO_4), (AsO_3), (CrO_4), and (F) cannot be present, since these acid-radicles form compounds with Ba which are insoluble in water. Ag excludes in addition the radicles (S), (Cl), (Br), and (I). Hence among the more commonly occurring acid-radicles, (NO_3) only need be tested for.

This example shows how much the examination for acid-radicles may often be simplified, when the metals which are present in a substance and the solubility of the substance are known.

1267. **Several Acid-radicles will also probably have been tested for in the Preliminary Examinations:** but in case the results have been interfered with by the presence of other substances, the analyst should refer to the reactions for acid-radicles (460 *et seq.*), and select decisive tests.

The Examination for Metals may also have yielded proof of the presence of certain acid-radicles. Thus:

A green alkaline solution, becoming purple when it is diluted or acidified (1236), shows	*Presence of* $(MnO_4)''$
A reddish-yellow solution, becoming green and depositing sulphur when H_2S is passed (1243), shows	*Presence of* $(CrO_4)''$
A purple solution, becoming colourless with H_2S (1243), shows . . .	*Presence of* $(MnO_4)'$
A yellow precipitate of As_2S_3 with H_2S, which appears only when the liquid is boiled (1244), shows . . .	*Presence of* $(AsO_4)'''$

An insoluble residue of SiO_2, after the filtrate from the H_2S-group has been evaporated to dryness (1245), shows . *Presence of* $(SiO_3)''$

And a yellow precipitate obtained with $AmHMoO_4$, before precipitating Group III. (1235), shows . . . . *Presence of* $(PO_4)'''$

If the presence of any of these acid-radicles has been detected in the above manner, its presence should, if necessary, be confirmed by a characteristic test.

Of the Acid-radicles which remain to be tested for, some can be detected by the plan drawn out in paragraphs 1268–1273, others are most easily found by applying special tests to the original substance (1274 *et seq.*).

SPECIAL TESTS FOR ACID-RADICLES IN THE Na_2CO_3-SOLUTION.

1268. **Removal of Metals.**—Before the following tests are applied, it is advisable to remove from the substance any metals, other than those of Group V., which it may contain, since some of them might be precipitated by the reagents which are added for the detection of the acid-radicles. If alkali-metals alone are present, this separation is unnecessary, since they are not precipitated by any of the reagents.

The removal of the metals may usually be effected by boiling a portion of the finely-powdered substance with pure Na_2CO_3-solution, which must be added to the clear solution as long as it causes any precipitate. The precipitated carbonates are then removed by filtration, and the clear filtrate is divided into five equal portions.

One of these portions is reserved in case of accident, and a second is kept for the tests for organic acid-radicles. The other three portions are acidified, while they are hot, by the addition of HCl, HNO_3 and $H\bar{A}$ respectively; they are then examined as is directed on the next page, a separate part being used for each test.

1269. **Certain Metals cannot be Completely Precipitated as Carbonates** by boiling the substance with Na_2CO_3-solution: the presence of these metals in the solution is, however, frequently of no consequence. If they must be precipitated, the addition of Am_2S, or the passage of H_2S, will usually separate them as insoluble sulphides; but the subsequent separation of the excess of Am_2S or H_2S, by gently warming the solution, is troublesome.

But since the analyst knows at this stage of the analysis what metals are present, it should not be difficult to separate them, or to allow for their presence while the tests for acid-radicles are being tried.

1270. The Three clear Acidified Portions of the Filtrate, obtained by boiling the substance with sodium carbonate-solution (1268), are tested by paragraphs 1271–1273. Further special tests (1274–1282) are then tried, if necessary.

Some general tests for organic acid-radicles occurring singly or together will be found in paragraphs 1343–1346.

1271. *Portion I. acidified with HCl.* Reagents added:—	*Present.*
$BaCl_2$-solution, a white precipitate insoluble on boiling (*Note* 1)	$(SO_4)''$
$BaCl_2$-solution, a semi-transparent precipitate insoluble on boiling (*Note* 2)	$(SiF_6)''$
AmCl and Am_2CO_3, a semi-transparent precipitate .	$(SiO_3)''$
$FeSO_4$-solution, a dark blue precipitate . . .	$(FeCy_6)'''$
$FeCl_3$-solution, a dark blue precipitate : $FeSO_4$ yielding a light blue precipitate	$(FeCy_6)^{iv}$
$FeCl_3$-solution, a red coloration, destroyed by pouring into $HgCl_2$-solution	$(CNS)'$

1272. *Portion II. acidified with HNO_3.* Reagents added:—	*Present.*
$AgNO_3$, a *pure white* precipitate, easily soluble in AmOH (*Note* 1)	(Cl)′, $(BrO_3)'$ (526), $(IO_3)'$ (531)]
$AgNO_3$, a *light yellow* precipitate, with difficulty soluble in AmOH	(Br)′
$AgNO_3$, a *yellow* precipitate, almost insoluble in AmOH	(I)′
Refer to *Notes* 3 and 4.	

1273. *Portion III. acidified with $H\bar{A}$.* Reagents added:—	*Present.*
$Pb\bar{A}_2$-solution, a yellow precipitate (*Note* 5)	$(CrO_4)''$
$CaCl_2$-solution, a white gelatinous precipitate	(F)′ (1281) or $(FeCy_6)^{iv}$ (1317)
$CaCl_2$, a white pulverulent precipitate .	$(C_2O_4)''$, probably.
$FeCl_3$-solution, a yellowish white precipitate	$(PO_4)'''$, or $(AsO_4)'''$ (1278, 279).

Note 1.—Unless the Na_2CO_3-solution, which was used in preparing the solution for these tests, was free from (SO_4) and (Cl), these acid-radicles, if detected, may have been present only as impurities in the Na_2CO_3 and not in the original substance; portions of the *original substance* should then be tested by paragraphs 1274, 1275.

Note 2.—The presence of (SiF_6) should be confirmed by adding KCl to

another part of the solution (468), or by heating the $BaSiF_6$ precipitate or the original substance with strong H_2SO_4 (469).

Note 3.—If $AgNO_3$ yields a black precipitate, this shows the presence of sulphide, or possibly of thiosulphate. Add HNO_3 and boil; the black Ag_2S will thus be decomposed, leaving a milky liquid, in which any other precipitate is readily seen after the sulphur has been coagulated by heating or by shaking the liquid.

Note 4.—If chloride, bromide and iodide have to be tested for, in the absence of CN (1211), the Na_2CO_3-solution is examined by pars. 564–566: or the precipitate produced by adding $AgNO_3$-solution in excess is treated as is directed in par. 563. It must be remembered that (CN), (CNO)′ $(FeCy_6)^{iv}$, $(FeCy_6)'''$ and (CNS) are also precipitated by $AgNO_3$. Accordingly, if cyanide has been detected (1211, 1271) the examination for acid-radicles precipitable by $AgNO_3$ must be conducted by 1283–1285.

Note 5.—If a white precipitate of $PbSO_4$ is produced here, it may be dissolved by adding AmOH in excess and warming the liquid (104); red basic lead chromate will remain if a chromate was present.

SPECIAL TESTS FOR ACID-RADICLES.

1274. **Sulphate.**—A portion of the original substance is boiled with HCl, and the liquid is decanted or filtered, if necessary, and is tested with $BaCl_2$; a white precipitate shows the *Presence of Sulphate.*

The presence of sulphide, sulphite and thiosulphate with sulphate may be detected by par. 1288.

1275. **Chloride.**—A portion of the original substance is warmed with HNO_3, and the solution is decanted or filtered, if necessary, and is tested by $AgNO_3$; a *perfectly white* precipitate, which is easily soluble in warm AmOH, shows the *Presence of Chloride.*

The presence of other acid-radicles which are precipitable by $AgNO_3$ is detected by pars. 1283–1285.

1276. **Nitrate.**—The clear aqueous solution or extract of the substance (*Note*) is mixed with its own volume of strong H_2SO_4, and the liquid is cooled. Freshly-made cold solution of $FeSO_4$ is poured upon the surface of the acid liquid without mixing; a brown layer or ring at the surface of contact of the liquids (509) shows the *Presence of Nitrate.*

Note.—If nitrite is present, it may be detected and removed as is directed in par. 525, or it may be removed by boiling the substance with excess of $H\bar{A}$ before the above test is applied.

Chlorate may be detected in the presence of nitrate by pars. 524 or 1287.

1277. **Cyanide,** if present, will have been detected by the special

test (1211), and by the smell of bitter almonds, given off by the substance after H_2SO_4 has been added (1226, Exp. 1).

Ascertain in what form cyanogen is present by paragraphs 1284, 1317.

1278. **Arsenate.**—This acid-radicle is unlikely to be present unless As has been detected during the examination for metals, in which the presence of (AsO_4) is rendered probable by the precipitation of yellow As_2S_3 occurring only when the acid liquid is boiled after it has been saturated with H_2S (1244).

If As has been found amongst the metals, proceed to test for (AsO_4) by adding HCl to a portion of the Na_2CO_3-solution (1268) until it is acid, then heating to expel CO_2; and adding AmCl, AmOH in excess, and $MgSO_4$. Filter off any precipitate which forms when the liquid is warmed and shaken, and pour a few drops of $AgNO_3$-solution upon the white precipitate on the filter; a change of colour to brown shows the *Presence of Arsenate.*

1279. **Phosphate.**—Boil some of the original substance with dilute HNO_3, and add *a little* of the clear solution to some $AmHMoO_4$-solution: stir the liquid well, and if no precipitate forms, warm *very gently*; a yellow precipitate shows the *Presence of Phosphate.*

If (AsO_4) has been detected (1278) the above test for (PO_4) is only trustworthy when the yellow precipitate has been obtained either in the cold or by employing a *very gentle* heat. If any doubt is felt concerning the presence of (PO_4), boil some of the original substance with H_2SO_3-solution (1239), and examine for PO_4 after the (AsO_4) has been entirely separated by passing H_2S into the boiling HCl-solution.

A precipitate which has been obtained with $AmHMoO_4$ may be further tested by dissolving it in AmOH, adding AmCl and $MgSO_4$, filtering, and dropping $AgNO_3$-solution upon the precipitate; if phosphate is present the white precipitate turns *yellow*, if arsenate is present the precipitate becomes *brown.*

1280. **Borate.**—Warm a portion of the substance with a little dilute HCl, dip into the solution a strip of turmeric-paper, and dry the paper in a steam-oven or at a gentle heat. The change of colour of the turmeric to *reddish-brown*, which becomes *blue-black* when the paper is moistened with AmOH, shows the *Presence of Borate.*

vessel for about ten minutes. Now remove the wax, and if the lines which were traced are etched upon the glass, the *Presence of Fluoride is shown* (654).

If SiO_2 is known to be present (1212), the test for fluoride must be made by conducting the gas, which is evolved when the substance is heated with strong H_2SiO_4, into dilute AmOH ; a deposit of gelatinous H_2SiO_4 proves the *Presence of Fluoride* (655).

1282. **Sulphide.**—If the presence of sulphide has been indicated by the tests in pars. 1221, 1226 or 1228, or if the presence of a sulphide is suspected and these tests have not detected it, the substance may be boiled with KOH-solution for some time, and alkaline $Pb\bar{A}_2$-solution may be added to the clear liquid; the appearance of a black precipitate or coloration indicates the *Presence of Sulphide.*

1283. **Cyanide, Chloride, Bromide and Iodide.**—The cyanide is first tested for by the Prussian-blue test (692) or by the thiocyanate test (693, 694).

If cyanide is found it may be removed by (*a*) or (*b*).

(*a*) Pass CO_2 through the slightly alkaline solution until the escaping gas is free from HCN and no longer gives a turbidity with a solution of $AgNO_3$ containing HNO_3.

(*b*) Mix the solution with $NaHCO_3$ and heat until the HCN ceases to be evolved in the escaping gas as tested by (*a*).

Chloride, bromide and iodide may now be tested for in the residual liquid, which will be free from cyanide, by par. 564, 565 or 566.

1284. **Cyanide, Ferrocyanide, Ferricyanide and Thiocyanate.**—Remove the cyanide as is described above (1283), testing the escaping gas for cyanide as is there directed.

Then acidify the liquid with HCl and add to one portion $FeCl_3$ in excess : a deep blue precipitate shows the *Presence of Ferrocyanide.* Filter off this precipitate : a red filtrate shows the *Presence of Thiocyanate.*

Add $FeSO_4$-solution to the rest of the acidified liquid : a dark blue precipitate indicates the *Presence of Ferricyanide.*

1285. **Chloride, Bromide and Iodide, with Cyanide, and Complex Cyanides :** add $AgNO_3$-solution in excess, filter, and dry and ignite the precipitate : all the cyanogen compounds will now have been decomposed, and the silver halides will remain practically unchanged. Heat the ignited precipitate with melted fusion mixture (563) and test the solution of the cool mass for chloride, bromide and iodide by pars. 564–566.

1286. Hypochlorite and Chlorate: test for hypochlorite by adding dilute H_2SO_4, when chlorine gas will be evolved in the cold (499).

Remove the hypochlorite by adding solution of NaOH and then solution of $MnSO_4$ (500):—

$$NaOCl + Mn(OH)_2 = MnO_2.H_2O + NaCl:$$

a brown precipitate of hydrated MnO_2 will form, filter this off and precipitate the chloride in solution by adding $AgNO_3$ in excess.

Filter off the AgCl, and add zinc and dilute H_2SO_4 to reduce the chlorate to chloride; then filter and add more $AgNO_3$, a white precipitate will indicate the original presence of chlorate.

1287. Chloride, Nitrate and Chlorate: test a portion of the solution for chloride by adding $AgNO_3$: a white precipitate shows the *Presence of Chloride.*

To the remainder of the solution add Ag_2SO_4-solution in excess to precipitate the chloride as AgCl: filter and boil the filtrate with KOH to expel any ammonium salts which may be present, add Zn-dust and boil again: if nitrate was present it will be reduced, and ammonia will be given off.

Filter off the residue, add HNO_3 in excess and $AgNO_3$: a white precipitate of AgCl shows that chlorate was originally present and has been reduced to chloride.

1288. Sulphide, Sulphite, Sulphate and Thiosulphate.—Remove the sulphide by shaking the solution with lead carbonate or with cadmium carbonate: the presence of sulphide will be shown by the lead darkening or the cadmium turning yellow.

Filter, and add $BaCl_2$ in excess to the filtrate to precipitate the sulphite and sulphate. Filter off the precipitate of these mixed barium salts, reserving the filtrate, and treat the precipitate with HCl to decompose the $BaSO_3$: a white residue denotes sulphate. Filter from the $BaSO_4$ and add to the filtrate Br-water and $BaCl_2$: a further white precipitate of $BaSO_4$ shows that sulphite was originally present.

The thiosulphate is tested for in the reserved filtrate from the mixed barium salts by acidifying it with HCl and warming: if yellow sulphur is precipitated and sulphur dioxide is produced, the presence of thiosulphate is shown.

crucibles are used the Teclu or the Méker burner (3) will give a sufficiently high temperature for most fusions.

Now pour some water into the cool crucible, and either allow it to stand, or boil the liquid, until the solid mass is loosened from the crucible. Boil distilled water in a porcelain dish with this mass, crushing it by pressure with a pestle if it does not quickly fall to pieces.

Allow the residue to settle, pour off the solution through a filter, and boil the residue with a little more water; then pour off the solution through the same filter, adding this filtrate to the former one.

The examination of the undissolved residue is described in paragraph 1309, and that of the filtrate in paragraph 1310.

1309. **Insoluble Residue on the Filter.**—Wash the residue well with boiling water, then make a hole in the bottom of the filter, and rinse the residue through into a test-tube by pouring upon it a little boiling dilute HCl (*Note* 1).

The residue will dissolve entirely when it is heated with the acid, if the fusion has been continued sufficiently long (*Note* 2). Filter, if necessary, and examine the solution by the General Table (1235), bearing in mind that only the metals in paragraph 1306 are likely to be present (*Note* 3).

Note 1.—**If Ag and Pb** are known to be present by the Preliminary Examination (1307, II.), dilute HNO_3 must be used instead of HCl for dissolving the residue.

If effervescence is produced by the action of the acid upon the residue, the presence of Ba, Sr, Ca, Mg is indicated.

Note 2.—If the residue does not wholly dissolve, either the fusion was incomplete or the residue was not thoroughly washed. The insoluble residue should therefore be dried again, then finely powdered and treated with fresh fusion-mixture (1308). If it consists of chrome iron ore, it may be dissolved by heating it with HNO_3 and $KClO_3$.

Note 3.—**The Solution should be Evaporated quite to Dryness** before Group III. is precipitated, and a water-bath should be used towards the end of the evaporation if the substance spirts: since if SiO_2 was present in the substance, the silicic acid may pass into the solution, and if it is not completely separated here by the process of evaporation (646), its presence may give rise to complications in the analysis.

1310. **Aqueous Solution of the Fused Mass.**—Divide this solution into two parts (**a**) and (**b**).

(**a**) Add HCl to one part until the liquid is distinctly acid, and evaporate in a porcelain dish to dryness, finishing the process on a water-bath, if necessary, to avoid spirting. Then continue to heat the dish gently over the flame or upon a sand-bath until the residue is quite dry: pour in a little strong HCl and warm, dilute and heat again; an insoluble residue shows :—**Presence of SiO_2.**

Filter off SiO_2 if necessary, and examine the filtrate by the General Table (1235). Al may be found here, but other metals, such as Cr, Mn, Zn, Sn, Sb, As, should also be tested for, since their oxides are soluble in alkalis, and may therefore pass into this solution.

(**b**) Test separate portions of the other part of the aqueous solution for the following acid-radicles as is described below. It must be remembered, however, that unless the fusion-mixture was free from chloride, sulphate and phosphate, the tests for these acid-radicles may be of little value.

Chloride: acidify with HNO_3 and add $AgNO_3$; white precipitate, easily soluble in AmOH.

Sulphate: acidify with HCl and add $BaCl_2$; white precipitate insoluble on boiling.

Chromate is indicated by the yellow colour of the solution, and its presence is confirmed by obtaining a yellow precipitate after acidifying with $H\bar{A}$ and adding $Pb\bar{A}_2$-solution. The chromium may have been present acting as a metal or as a constituent of the chromate acid-radicle (*Note* 3, 1255).

Phosphate: acidify with HNO_3, add a few drops to some $AmHMoO_4$-solution, and warm gently; a yellow precipitate forms, often only after a time or when the liquid is gently heated.

If As has been found when H_2S was passed into the hot HCl-solution, the presence of (PO_4) must be confirmed in a portion of the filtrate from which the As has been completely precipitated (1279), else the above yellow precipitate may have been due to (AsO_4).

Fluoride: add HCl in excess to a part of the solution, stir well, and let stand until the CO_2 has escaped; then add AmOH in excess, then $CaCl_2$-solution as long as it produces any precipitate, and let stand for a time. Filter off and dry any precipitate which forms, and pour strong H_2SO_4 upon it in a platinum or lead crucible covered with a suitably prepared watch-glass (654).

1311. **Examination for K, Li and Na.**—Since K and Na have been introduced into the substance by the fusion-mixture, these alkali-metals cannot be tested for in the aqueous solution obtained after fusion.

Unless the analyst is satisfied that the spectroscopic test, made with the special precautions mentioned in paragraph 67, is conclusive, he should proceed to examine the substance for K, Li and Na by paragraph 1313.

The simpler method of examination by paragraph 1315 may be employed if the substance is a silicate: and if K, Li and Na are present in a condition in which they are insoluble in acids, they will usually be contained in a complex silicate.

ANALYSIS OF SILICATES.

1312. **The Presence of Silica** in a substance will have been shown by the special test (1212) or by VIII. in paragraph 1307. When silica has been found it becomes necessary to examine the substance for all metals, since many silicates, which are soluble when they are alone, become insoluble when they are mixed or combined with other insoluble silicates.

Many silicates may be entirely decomposed by heating them with strong HCl for some time just short of boiling. If the decomposition has been complete, only a colourless residue of silicic acid will remain, which may be identified by its insolubility in fused microcosmic salt (648), and by causing effervescence when it is fused into a bead of Na_2CO_3 (649).

If it is found that the silicate is not completely decomposed by hot strong HCl, it should be treated with fused alkaline carbonates, as is directed in paragraphs 1308, *et seq.* In the examination which follows the fusion, it must be remembered, however, that all metals may be present, and that the metals Na and K must be tested for specially in the original substance by paragraph 1313 or 1315, since they have been introduced in the fusion-mixture.

EXAMINATION FOR K, LI AND NA IN AN INSOLUBLE SUBSTANCE.

Since Na and K cannot be tested for in the solution which is obtained after fusion with alkaline carbonates (1308), a separate portion of the original substance must be examined for these metals by one of the two following processes. The materials which are used in the tests must be perfectly free from K and Na.

1313. **Decomposition by means of CaO.**—The finely-powdered substance is mixed with its own weight of sublimed and crystallised NH_4Cl in powder, and with eight times its weight of pure $CaCO_3$ (1314). The mixture is gently heated in a platinum crucible for a few minutes, and is finally kept at a bright red heat for twenty or thirty minutes. The mass will not fuse as a whole, but sufficient CaO will be dissolved by the fused $CaCl_2$, and thus be brought into contact with the silicates, to secure their decomposition.

The cool substance is turned out of the crucible if possible, and is boiled with water for some time after it has crumbled by the slaking of the CaO. The liquid is then filtered, and Am_2CO_3-solution is added to the filtrate until it causes no further precipitate of $CaCO_3$. The filtrate from this precipitate is evaporated considerably, and is then freed from traces of Ca by the addition of $Am_2C_2O_4$.

1317. Boil a portion of the substance for several minutes with NaOH-solution in a porcelain dish, in order to convert the various cyanides into soluble sodium salts. Since this solution may contain the metals Al and Zn, add Na_2CO_3-solution as long as it causes any precipitate, and boil again for several minutes: then filter, make the cold filtrate just acid with HCl, filter if necessary, and test separate portions as follows :—

Reagent added.	Result.	Inference.
1. $FeSO_4$-solution, freshly prepared	Blue precipitate . .	Presence of ferro- or ferri-cyanide.
	White precipitate . .	Probable presence of cobalti-cyanide.
2. $FeCl_3$-solution	Blue precipitate . .	Presence of $(FeCy_6)^{iv}$.
	Blood-red coloration seen on filtration	Presence of $(CNS)'$.
3. Add $ZnSO_4$-solution as long as it causes any precipitate	Light brown precipitate	Presence of $(FeCy_6)'''$.
	White precipitate . .	Presence of $(FeCy_6)^{iv}$. $(CoCy_6)'''$.
The precipitate produced by $ZnSO_4$ should be filtered off and fused into a colourless borax bead.	A blue bead is produced	Presence of $(CoCy_6)'''$.

1318. **If a Simple Cyanide only is present,** the ordinary course of analysis (1229 *et seq.*) is pursued, but it will be necessary to remove the HCN by boiling the solution for some time after adding an acid (1229, 1236).

1319. **If Thiocyanate only is found** by the above preliminary tests (1317), it may usually be decomposed completely, as is proved by testing a portion with $FeCl_3$-solution, by pouring on the substance which is to be examined for metals some strong HNO_3 in a porcelain dish and boiling down nearly to dryness. The liquid is then diluted and boiled, and may be considered as Solution III. (1229), any undissolved residue being treated as is there directed.

The less simple methods in paragraph 1321 may be employed instead.

1320. **If the Presence of Ferro-, Ferri-, or Cobalti-cyanide has been proved** by the preliminary tests (1317), two methods of procedure are open to the analyst.

Either the cyanogen may be removed from the substance before commencing the analysis (1321); or the substance may be examined without any such preliminary treatment (1322).

The advantage of employing the more complicated method (1322) is that it enables the analyst to decide whether the metals are present in complex cyanogen acid-radicles or not. It also yields a more precise knowledge of the constitution of the substance.

METHOD I.

1321. The Removal of the Cyanogen from the Substance may be effected by either of the following processes, 1 or 2. The substance may then be examined for metals in the usual way (1235).

1. Pour upon the powdered substance strong H_2SO_4 in a porcelain crucible, evaporate to dryness and heat the residue until the evolu-

METHOD II.—FOR

1322. Boil the substance with water, filter, and wash the residue

<table>
<tr><td rowspan="4">Filtrate: examine this for metals, more especially the alkali-metals, and for acid-radicles, according to the directions given for analysing a liquid (1213).
The acid-radicles should be first tested for in a portion of the solution, and if $(FeCy_6)^{iv}$, $(FeCy_6)'''$, $(CoCy_6)'''$, one or more are found, the solution must be evaporated to dryness with HNO_3, and the residue strongly heated (General Table 1235) after filtering from the H_2S precipitate, in order to destroy these cyanogen radicles.
The Fe, Co, etc., in the cyanogen acid-radicles will then be detected in the General Table (1235).</td><td colspan="3">Residue: boil in a porcelain dish with KOH-solution for several minutes, boil again; filter and wash the residue :—</td></tr>
<tr><td colspan="3">Filtrate: pass H_2S, and if it causes any precipitate continue to pass the filter :—</td></tr>
<tr><td colspan="2">Precipitate: wash well with boiling water, and boil the precipitate with strong HNO_3, a black residue of HgS may remain, filter this off after diluting the acid, and confirm the presence of Hg in the precipitate by heating it with Na_2CO_3 in a bulb-tube (140) or by par. 1250.
The filtrate (or solution if HgS is absent) is evaporated to dryness, the residue is then dissolved in a little hot strong HCl, the solution is much diluted, saturated with H_2S, and filtered :—</td><td>Filtrate: add dilute HNO_3</td></tr>
<tr><td>Precipitate: examine for Pb and Cu by Table II. (1253).</td><td>Filtrate: add AmCl, AmOH in excess, and Am_2S, and examine for Zn, Mn, Ni, Co, etc. (1296).</td><td>Precipitate: boil with KOH, filter off any black precipitate and examine it for Hg by heating it with Na_2CO_3 in a bulb-tube (140), or by par. 1250.
Add to the filtrate or solution HCl until it is acid, pass H_2S to saturation, and examine for As, Sb, Sn, (Pt, Au), by Table II., commencing at par. 1254.</td></tr>
</table>

Note.—If H_2S causes a precipitate, NaHS or KHS may be added, drop by dro be done instead of passing H_2S to saturation and then adding KOH.

tion of H_2SO_4-fumes cease. When the residue is cold, heat it with a little strong HCl, then add water and heat again until all is dissolved, except possibly $BaSO_4$ and $SrSO_4$ which are found by par. 1245.

2. Heat the substance strongly in a porcelain crucible after mixing it with three or four times its weight of a mixture of three parts of Am_2SO_4 and one part of $AmNO_3$.

METALS IN CYANOGEN COMPOUNDS.

with boiling water, adding the washings to the filtrate :—

<table>
<tr><td colspan="4">then add Na_2CO_3-solution as long as it causes any precipitate in the solution or the filtrate, and</td></tr>
<tr><td colspan="3">gas until the liquid is saturated, then add more KOH (Note), heat and</td><td rowspan="4">Residue : dissolve (1229) and examine for metals in the usual manner (1235).
Fe, Co, Mn, Cr, if found in this residue, were not present in cyanogen acid-radicles.</td></tr>
<tr><td colspan="3">gradually until the liquid is just acid, pass H_2S to saturation and filter :—</td></tr>
<tr><td colspan="3">Filtrate : Divide into two parts, a, b :—</td></tr>
<tr><td rowspan="2">a. Examine for acid-radicles in the usual way, testing for $(CoCy_6)'''$ by adding excess of $ZnSO_4$, filtering and trying whether the precipitate gives a blue bead with borax.</td><td colspan="2">b. Evaporate to dryness and fuse the residue : when cold, boil it with water and filter :—</td></tr>
<tr><td>Residue : dissolve in HCl, and test for Al, Fe, Mn, Co (1296) ; the last three if found were present as cyanogen acid-radicles.</td><td>Filtrate : acidify a portion if yellow, with $H\bar{A}$ and add $Pb\bar{A}_2$, a yellow precipitate shows $(CrO_4)''$, the Cr having been present as cyanogen acid-radicle.
Test another part for Al by adding HCl in excess, then AmOH in slight excess.</td><td></td></tr>
</table>

until it no longer gives any precipitate in the liquid or in the filtrate ; this may

This table runs across both pages.

1323. GENERAL GROUP TABLE FOR

Group I.—Reagent HCl.	*Group II.*—Reagent H_2S.
The Group-Pp. may contain in addition to $AgCl$, Hg_2Cl_2, $PbCl_2$:— *TlCl* (*white*). H_2WO_4 („). *TlCl* will usually be readily detected by a spectroscopic examination of the original substance or of the group-pp. It may be removed from the group-pp. by boiling with a little water, and ppd. from the cold filtrate by KI (Pb is also thus ppd.): the pp. is yellow, and gives the thallium spectrum. H_2WO_4: a white pp., becoming yellow when the liquid is boiled. Its presence is confirmed by dropping a piece of Zn into a portion of the acid liquid and pp., when a *deep blue* colour will be obtained. Also by fusion of the pp. in a microcosmic bead, which will be *colourless* or *yellow* in the outer flame, *blue* (or with $FeSO_4$, *blood-red*) in the inner flame.	*The Group-Pp. may contain as sulphides, in addition to sulphides of Hg, Pb, Bi, Cu, Cd :—* *Pd*-sulphide (*black-brown*), *Tl*-sulphide (*black*), [*Os, Rh, Ru**-sulphides] — Insoluble in Am_2S. *And in addition to SnS, SnS_2, Sb_2S_3, As_2S_3, Au_2S_3, PtS_2 :—* [*Ir*-sulphide*], *Mo*- „ (*brown*), *Se*- „ (*red-yellow*), *Te*- „ (*black*) — Soluble in Am_2S. The *yellow* colour of a solution containing V is changed to *blue* by H_2S. *Tl* is readily found by the spectroscope in the original substance or in the group-pp. *Pd* will remain in solution in excess of AmOH with Cd and Cu in Table II.A. (1253): from this solution it is ppd. by adding HCl: its presence may be further confirmed by the $HgCy_2$-test (213), or the KI-test (214). The examination of the sulphides in Group II.B., when the above elements may be present, is best commenced by fusion with Na_2CO_3 and Na_2O_2 or $NaNO_3$. From the cooled mass, water dissolves sodium-arsenate, -molybdate, -selenate, and -tellurate, leaving SnO_2, sodium-antimonate, Au, Pt, and Ir undissolved; the elements may then be detected by special tests. For the separation and detection of the platinum metals a special work must be consulted. * Only completely ppd. if the liquid has been warmed, and H_2S passed for a long time.

PRECIPITATION OF RARER ELEMENTS.

Group III.—Reagents AmCl, AmOH, and Am_2S.	Precipitated from the filtrate from Group III. by excess of HCl.	*Group V.*
The Group-Pp. may contain as sulphides, in addition to Fe, Zn, Mn, Ni, Co:— *U* (*black brown.*) *In* (" ") *Tl* (" ") *And as hydroxides in addition to Al, Cr (and phosphates, etc.):—* *Ti* (*white, flocculent*). *Be* (*colourless, gelatinous*). [*Zr* " "]. [*Ta, Nb, Ce, La, Di, Yt, E, Th.*]	*As sulphides:—* *V* (*black*). *W* (trace, *brown*). *Ni* (trace, *black*).	The filtrate, after the separation of all the group-precipitates, may contain besides Mg, K, and Na:— *Li, Cs, Rb.*
Tl and *In* will usually be readily detected by a spectroscopic examination of the pp. *Tl* may be first separated and detected by dissolving some of the group-pp. in boiling dilute HCl, and reducing any Fe present in the solution by H_2SO_3; then precipitating Tl by addition of KI, and testing the pp. by the spectroscope. A more complete scheme for the analysis of this group-pp. will be found in par. 1324.	This pp. is dried and then fused with a mixture of Na_2CO_3 and KNO_3: on boiling the mass with water, NiO remains undissolved; it is filtered off, and its presence confirmed by fusion in a borax bead (313). The aqueous solution may contain alkaline vanadate and tungstate. V is separated by saturating the liquid with AmCl, and its presence confirmed in the pp. by the borax bead (397), and by dissolving the pp. in HCl and employing the reactions with H_2O_2 and with Zn (396, 393). The filtrate, after concentration if necessary, is acidified with HCl, and the presence of W confirmed by the Zn-reaction and the microcosmic bead (128, 131)	These metals are readily detected by their very characteristic spectra (66). Before proceeding to the spectroscopic examination, it is well to remove the Mg and to convert the alkali-metals into chlorides by the procedure given in the second paragraph of *Note* 3 (1263). Pour a few drops of HCl upon the residue thus obtained, and evaporate the solution almost to dryness; triturate the residue with 90 per cent. alcohol, and filter. The alcoholic filtrate will contain all the Li, Rb and Cs, with small quantities of K and Na. If traces of Rb and Cs only are present, evaporate and extract with alcohol several times. Evaporate the alcoholic extract to dryness, add a little strong HCl, evaporate once more, gently ignite, and triturate the residue with equal parts of anhydrous ether and absolute alcohol: then filter through a dry filter. The filtrate which contains the Li may be evaporated to dryness and tested by the flame coloration and the spectroscope (66). The residue is dissolved in a little HCl, and K, Rb and Cs are ppd. by H_2PtCl_6: this pp. is boiled with small quantities of water until it no longer gives the K spectrum, the spectra of Rb and Cs will, if present, be given by the residue.

1324. TABLE FOR ANALYSIS OF GROUP III. PRECIPITATE,

The precipitate may contain Fe, Tl, Al, Cr, Zn, Mn, Ni,

These lines run across both pages.

<table>
<tr><td colspan="4">After a preliminary spectroscopic examination has been made of a small portion of the pp. for Tl and the group pp. is dried and fused in platinum with $KHSO_4$ for some time, the cold mass is then pow-</td></tr>
<tr><td rowspan="6">Residue: may contain Ta_2O_5, Nb_2O_5, also SiO_2, and traces of Fe and Cr which have escaped solution.
By fusion with $KClO_3$ and NaOH, Cr and Si are rendered soluble in dilute NaOH; from the residue, insoluble in NaOH, Ta_2O_5 and Nb_2O, may be removed by washing with dilute Na_2CO_3-solution.</td><td colspan="3">Solution: reduce Fe by adding H_2SO_3 in excess, dilute considerably and passing a stream of CO_2 unless it smells constantly of SO_2:—</td></tr>
<tr><td rowspan="5">Pp. may consist of TiO_2, possibly also traces of Zr.
Confirm the presence of TiO_2 by the microcosmic bead (339).</td><td colspan="2">Filtrate: add a few drops of strong HNO_3, concen- more by adding excess of AmOH:—</td></tr>
<tr><td colspan="2">Pp. may contain Fe, In, U, Cr, Al, Be, etc. Dissolve</td></tr>
<tr><td colspan="2">Pp. may contain Fe, In, U, etc. Dissolve in HCl, of HCl, add $BaCO_3$, and let stand:—</td></tr>
<tr><td rowspan="2">Pp. may contain Fe, In, U, also traces of Al and Cr.
It is dissolved in HCl, and $NaHCO_3$ is added in excess, whereby U is obtained in solution.
In is found by the spectroscope.</td><td>Filtrate may contain Zr, Ba is pp^{d.} by adding liquid is concentrated, with KOH. Crystals the liquid is allowed The pp. is washed with</td></tr>
<tr><td>Pp. may contain Zr, Th, Ce.
Th and Ce are dissolved away by boiling with dilute HCl, and are repp^{d.} by AmOH.</td></tr>
</table>

WHEN THE RARER ELEMENTS MAY BE PRESENT.

Co, Ta, Nb, E, Be, Ti, Ce, La, Zr, Th, Yt, In, U, Di.

In, and Tl has been further tested for, if necessary, by KI as directed in the General Table (1323), dered and allowed to stand, with shaking, for a long time with cold water :—

boil for a long time, preserving the liquid from oxidation by the air by covering the vessel, and by

trate by evaporation, and add AmOH in excess : filter, dissolve the pp. in HCl, and precipitate once

it in HCl, and add excess of cold strong KOH-solution :—

Filtrate may contain :— Zn, Mn, Ni, Co.

boil off any large excess

Ce, La, Di, Yt, E, Th. excess of H_2SO_4, the and exactly neutralised of K_2SO_4 are added, and to stand for some hours. K_2SO_4-solution.

Soln. may contain Y, E, also Be. The solution is ppd. by AmOH, and Be dissolved away from it by $H_2C_2O_4$.

Filtrate may contain Al, Cr, Be : dilute and boil for some time, filter. Al remains in solution, and may be ppd. by adding HCl just in excess, then AmOH in excess.
Cr and Be are separated by fusion with Na_2CO_3 and $KClO_3$, dissolving in water and ppg., Be by adding HNO_3 in excess, then AmOH in excess.

GENERAL METHODS FOR DETECTING ORGANIC SUBSTANCES.

INTRODUCTORY REMARKS.

1330. **The Detection and Identification of an Organic Substance** is usually more difficult than the detection of an inorganic substance, and the difficulty is increased when a mixture of organic substances has to be dealt with.

Since no complete scheme of separation is possible, recourse must be had to several partial separations, such as the precipitation of one or more of the substances in an insoluble form, or the use of a suitable liquid which is a solvent for certain substances but not for others. Sometimes separation may be effected by the application of heat, the more volatile substance passing off as vapour and leaving the non-volatile substance behind. Fractional distillation (672) may be utilised for the separation of liquids of different boiling-points; distillation in steam and *in vacuo* may also be resorted to.

The suggestions and Tables which are given below include :—

(1) Preliminary tests, such as the action of heat, acids and other reagents.

(2) The identification of the elements present.

(3) The identification of the compounds by their special properties and tests.

The student should be familiar with the methods of detecting the elements in an organic substance (673–688), and with the reactions and properties of organic substances (689–1148) before he applies them in the following scheme.

SCHEME FOR THE DETECTION OF ORGANIC SUBSTANCES.

PRELIMINARY EXAMINATION.

1331. **The Physical Properties of the Substance,** such as its colour and smell, are noted; also its physical condition, and, if solid, whether it is amorphous or crystalline.

The determination of its solubility in various solvents will frequently indicate the chemical character of the compound, since :—

Organic salts are usually soluble in water, but insoluble in ether.

Organic acids are often soluble in hot water, but sparingly soluble in cold water, and are soluble in alcohol and in ether.

Hydrocarbons and their haloid derivatives are insoluble in water, but soluble in ether.

Alkaloids and organic bases are usually insoluble in water, but soluble in acids and in organic liquids.

The Table of Solubilities (1336) will be of use after trying the action of solvents.

A knowledge of the melting-point (669), boiling-point (671), and density (668) is also often of great assistance.

Note also the effect produced by the substance or its solution on litmus. Acid reaction usually indicates the presence of free acids, or of hydrolysed salts of certain bases; esters also usually contain free acid. Many alkaloids and basic substances have an alkaline reaction to test-paper; but a large number of organic bodies such as the hydrocarbons, alcohols and ethers are neutral in reaction.

1332. **Ascertain what Changes the Substance undergoes when it is heated in a Test-tube,** whether it is volatile or fusible, and whether any gases or vapours are evolved.

EFFECT OF HEATING THE SUBSTANCE IN A TEST-TUBE.

Result.	Observation.	Inference.
a. The substance volatilises, leaving no residue.	The vapour is non-inflammable.	Chloroform.
	The vapour burns with a pale blue flame.	Alcohols, aldehydes.
	The vapour burns with a blue flame.	Chloral, carbon disulphide.
	The vapour burns with a pale blue flame; slight charring occurs.	Glycerol.
	The vapour burns with a smoky flame.	Aniline, benzene, naphthalene, turpentine.
	The vapour burns with a luminous flame.	Ether, ethyl acetate, benzaldehyde, nitrobenzene.
	The vapour is acid, pungent, and inflammable.	Formic acid, acetic acid.
b. The substance fuses, and volatilises without residue.	The vapour burns with a smoky flame.	Phenol.
	NH_3 and CO_2 formed.	Urea.
	Pungent fumes yielding a white sublimate.	Oxalic acid, succinic acid.
	Pungent fumes, burning with a smoky flame; and a sublimate is formed.	Benzoic acid.
	A slight explosion.	Picric acid.
c. The substance fuses and chars.	It chars slowly, evolving CO.	Formate.
	It chars slowly, evolving acetone.	Acetate.
	It emits a smell of charred sugar.	Tartrate, citrate, malate, meconate, pyrogallol, sugars.

Result.	Observation.	Inference.
e. The substance neither chars nor fuses.	A carbonate remains (474).	Oxalate.
f. The substance fuses to a coloured liquid.	The liquid is reddish; vapour of unpleasant smell is emitted, which burns with a smoky flame.	Hippurate, or an alkaloid.
g. The substance fuses, and evolves cyanogen.	No further special observations. A smell of H_2S is also noticed. The substance darkens in colour.	Cyanide. Thiocyanate. Ferrocyanide, or ferricyanide.

1333. **Heat the Substance with free exposure to the Air** on a piece of thin porcelain, or on a nickel spatula : if a black residue of carbon is left, burn off the carbon by heating it strongly from beneath in the blowpipe-flame (Exp. 21, page 39).

One of the following results may be obtained :—

(*a*) *A Coloured Residue* may remain and will probably be due to the presence of a metal which produces a coloured oxide.

(*b*) *A White Residue* may remain, which when it is moistened with water shows an alkaline reaction to test-paper : this may be caused by the oxide or carbonate of K, Na, Ba, Sr, Ca, or Mg derived from an organic salt.

The residue, in either case, may be examined by the preliminary tests 1219, 1220, and may then be dissolved (1229) and examined by the General Table (1235).

1334. **Mix the Substance with powdered Soda-lime and heat,** noting carefully the characteristic smell of any of the following substances, which may be also recognised by special tests :—

(*a*) *Ammonia* (426), is evolved from nitrogenous substances, such as ammonium-salts, urea, alkaloids, urate and hippurate.

Nitrocompounds, such as nitrobenzene and picrate, do not give off ammonia when they are heated with soda-lime.

(*b*) *Aniline* (978), evolved from aniline compounds.

(*c*) *Benzene* (814), evolved from benzoate or hippurate.

(*d*) *Phenol* (848), evolved from salicylate.

1335. **Try the Action of Strong Sulphuric Acid upon the Substance,** both in the cold and on heating : the results which may be obtained are tabulated below :—

This test may be supplemented by heating the substance with *dilute* H_2SO_4, since formates, acetates and cyanogen-compounds may be frequently detected by this means.

EFFECT OF ADDING STRONG H_2SO_4 TO THE SUBSTANCE, OR TO ITS STRONG SOLUTION, AND THEN HEATING.

Result.	Observation.	Inference.
a. No change occurs in the cold, and either little or no charring on heating.	CO evolved, no charring.	Formate.
	HĀ evolved, no charring.	Acetate.
	CO and CO_2 evolved, no charring.	Oxalate.
	Pungent fumes, no charring.	Chloral; chloroform.
	Slowly darkens, irritating fumes evolved.	Succinate, or benzoate.
	Slowly darkens; acid fumes, then CO and CO_2 evolved.	Malate.
	Slowly darkens; CO and CO_2 evolved. (Difference from tartrate, etc.)	Citrate.
	Slowly darkens; pungent fumes evolved.	Urea.
	Effervesces, slowly darkens.	Urate.
	HCN evolved, no charring.	Cyanide.
	HCN and finally CO evolved, white precipitate.	Ferricyanide.
	CO evolved, and liquid becomes turbid.	Ferrocyanide.
	SO_2 evolved, yellow S formed.	Thiocyanate.
	Slight charring.	Meconic acid.
b. No change occurs in the cold, but the substance turns dark-coloured, or chars, when it is heated.	Fragrant smell; vapour burns with a smoky flame; SO_2 is evolved, and charring occurs.	Alcohols.
	Acrolein is smelt, and ultimately SO_2 is evolved with much charring.	Glycerol.
	CO and SO_2 are evolved, with gradual charring.	Most sugars.
	CO, CO_2, and SO_2 are evolved, with rapid charring.	Tartrate.
	SO_2 is evolved, and charring occurs.	Hippurate.
	The substance then turns reddish-brown, evolving CO_2 and pungent fumes.	Salicylate.
	The substance turns brown, and SO_2 is evolved.	Tannate.
	A vivid red coloration is produced, and SO_2 is evolved.	Gallate.
	Characteristic smell, then charring, and evolution of SO_2.	Turpentine.
c. The substance usually becomes coloured in the cold; the colour deepens on heating.	Colourless or pale brown, cold; blackening on heating.	Quinine, cinchonine, strychnine, etc.
	Yellow, cold; puce, on heating.	Narcotine.
	Pink, cold; blackening on heating.	Brucine.
	Colourless, cold; blue on heating.	Codeine.
	Colourless, cold; violet on heating.	Papaverine.
	Pink, cold; violet, then brown on heating.	Morphine.
	Yellow, cold; brown-red, then violet on heating.	Narcotine.
	Yellow, cold; red on heating.	Veratrine.
	Blood-red coloration, cold.	Salicin.
	Yellow, brown and finally red coloration.	Digitalin.
	Forms white sulphate, soluble in excess.	Aniline, pyridine, quinoline.
	Yellow, cold; charring on heating, and evolving CO and SO_2.	Starch.
	Brown, cold; charring rapidly, and evolving CO and SO_2. *Solid* cane-sugar gives these changes slowly.	Cane-sugar.

1336. Test if the Substance is Soluble in or Miscible with :— (1) Cold water, (2) Hot water, (3) Alcohol, (4) Ether.

The knowledge of the solubility of the substance may aid in its detection, and may further enable a separation of mixed substances to be effected by the use of suitably selected solvents.

TABLE OF SOLUBILITY OF ORGANIC SUBSTANCES.

s = soluble.
i = insoluble.
ss = slightly soluble.
vs = very soluble.
vss = very slightly soluble.

Substance.	Water.		Alcohol.	Ether.
	Cold.	Hot.		
ACIDS :—				
Aliphatic :				
Formic	vs	vs	vs	i
Acetic	vs	vs	vs	s
Oxalic	s	vs	vs	s
Succinic	ss	vs	s	ss
Malic	vs	vs	vs	vss
Tartaric	s	s	s	i
Citric	s	s	s	i
Aromatic :				
Benzoic	ss	s	s	s
Salicylic	ss	s	s	vs
Gallic	ss	s	s	s
Tannic	s	s	ss	vss
Hippuric	—	s	s	ss
Meconic	ss	s	s	vss
Uric	vss	vss	ss	i
HYDROCARBONS, AND DERIVATIVES :—				
Turpentine	i	i	vs	vs
Benzene		i	s	s
Naphthalene	i	i	vs (hot) vss (cold)	s
Anthracene	i	i	ss	ss
Chloroform	i	i	s	s
Carbon tetrachloride	i	i	—	—
Iodoform	i	i	s!	s!
Carbon disulphide	i	i	vs	vs
ALCOHOLS, ETHERS :—				
Methyl alcohol	vs	vs	vs	vs
Ethyl alcohol	vs	vs	vs	vs
Amyl alcohol	vs	vs	vs	vs
Glycerol (Glycerine)	s	s	s	i
Ethyl ether	ss	ss	vs	vs
Ethyl acetate	vs	vs	vs	vs
PHENOLS :—				
Phenol (Carbolic acid)	s	s	vs (hot)	s
Hydroquinone	s	s	s	s
Pyrogallol (Pyrogallic acid)	vs	vs	vs	s
Trinitrophenol (Picric acid)	vss	s	s	s
ALDEHYDES, KETONES :—				
Formaldehyde	ss	ss	s	i
Acetaldehyde	vs	vs	s	s
Trichloraldehyde (Chloral)	s	s	s	—
Benzaldehyde	s	s	vs	vs
Acetone (Dimethyl ketone)	s	s	s	s
CARBOHYDRATES :—				
Dextrose (Grape sugar)	vs	vs	s	s($CH_3.OH$)
Laevulose (Fructose)	s	s	s	—
Sucrose (Cane sugar)	vs	vs	ss	i
Maltose (Malt sugar)	s	s	s	i
Lactose (Milk sugar)	ss	ss	vss	i
Cellulose	i	i	i	i
Starch	i	s	i	i
Dextrin	s	s	i	i

Substance.	Water.		Alcohol.	Ether.
	Cold.	Hot.		
GLUCOSIDES :—				
Salicin	vss	s	s (hot)	i
Digitalin	ss	ss	s	vss
Amygdalin	s	—	s (hot)	i
ORGANIC BASES :—				
Aniline	vss	vss	s	s
Toluidine	ss	s	vs	—
Pyridine	miscible	miscible	—	—
Quinoline	vss	vss	s	s
Acetanilide (Antifebrin)	ss	ss	i	i
Phenacetin	i	vss	ss	i
Antipyrin (Phenazone)	s	s	s	ss
Urea (Carbamide)	vs	vs	vs	ss
ALKALOIDS :—				
Quinine	i	i	vss	ss
Cinchonine	i	i	ss	vss
Morphine	vss	vss	s	vss
Codeine	s	s	vs	i
Narcotine	i	i	ss	s
Papaverine	i	i	ss	i
Strychnine	i	i	s (hot)	i
Brucine	ss	ss	s	i
Caffeine (Theine)	ss	s	ss	vss
Cocaine	ss	ss	s	s
Veratrine	i	i	s	s
Atropine	i	i	vs	s
Hyoscyamine	ss	ss	vs	s
Hyoscine	ss	ss	s	s
Nicotine	vs	vs	vs	vs
Coniine	ss	s	vs	vs

SPECIAL EXAMINATION OF ORGANIC SUBSTANCES.

1337. If the substance is a simple one, it will probably have been identified by the preceding preliminary examination, and it will then be at once submitted to confirmatory tests.

But if the preceding treatment has given any indication that the substance is a mixture, some method of separation should be devised. The action of solvents (1336), or treatment with solutions of acids or of alkalis may be tried upon a solid substance. A liquid may be subjected to fractional distillation (672).

In any case it is advisable to ascertain what elements are present in the substance: the presence of the more important elements will be indicated by the following experiments.

1338. Heat the dry Substance strongly in a Test-tube with dry CuO (674, 676), and observe the results :—

(*a*) CO_2 is evolved (474), whereas the original substance evolved no CO_2 when it was treated with dilute HCl, indicating the *Presence of C.*

(*b*) Drops of water condense on the inside of the tube, indicating the *Presence of H.*

1339. Heat the Substance with a little Sodium in an ignition-tube until it is charred, and drop the tube into a few c.c. of water contained in a mortar: then grind up the fragments with the

water, filter, and divide the filtrate into three portions:—

(*a*) To the first portion add a small crystal of $FeSO_4$, boil the liquid and acidify it with HCl: a blue or green coloration shows the *Presence of N* (679).

(*b*) In the second portion dissolve a small crystal of sodium nitroprusside: a violet or purple colour shows the *Presence of S* (681).

(*c*) *If the substance contains no nitrogen,* add to the third portion HNO_3 and $AgNO_3$-solution: a white or yellow precipitate shows the *Presence of Cl, Br, I* (688).

(*d*) *If the substance contains nitrogen,* ignite a fresh portion with soda-lime free from chloride in a combustion-tube. Shake out the contents of the tube into dilute nitric acid, filter the liquid and add $AgNO_3$-solution; a white or yellow precipitate shows the *Presence of Cl, Br, I* (688).

1340. **Mix the charred Substance with Mg-powder,** heat the mixture strongly and moisten the cold residue: an onion-like smell indicates the *Presence of P* (684).

1341. **Hydrolysis** may be resorted to for the identification of certain substances, such as esters, alkyl cyanides, glucosides and sugars, which may by this means be split up into readily recognisable products. The process consists in the prolonged heating of the substance with a moderately strong acid, such as HCl or H_2SO_4, or with KOH-solution. The process may be carried out in a flask connected with a reflux condenser.

The resultant products include alcohols, glucoses and organic acids, and these may be detected by the methods given under the separate tests and reactions for these substances.

1342. **The Presence of an Alkaloid** may be ascertained by the application of the general tests given in paragraphs 1036–1042. The identification of the particular alkaloid present may then usually be effected by carefully extracting with warm pure alcohol acidified with dilute HCl, driving off the excess of alcohol, diluting the extract with water and [illegible]ng the solution by paragraphs 1050–1148.

A more general method for separating the alkaloid consists in making the mixture alkaline with NaOH-solution, evaporating the whole to dryness, and extracting the residue several times with small quantities of ether. The ether is then distilled off, and the residue consists of the alkaloid free from inorganic and from most organic substances (*Note*). If aniline, pyridine or quinoline are present it will be necessary to remove them by steam distillation: acetanilide, phenacetin, antipyrin and digitalin are soluble in ether and may also be present.

Note.—Morphine is insoluble in ether; but this alkaloid may be extracted by hot amyl alcohol from the residue remaining after the extraction by ether

1343. The Presence of Organic Acids or their Salts in solution can usually be determined by the formation of characteristic insoluble compounds on the addition of solution of a salt of iron, calcium, or silver (1344, 1345, 1346).

The organic acid-radicles should be present in sodium, potassium, or ammonium salts, since other metals interfere more or less seriously with the detection of the acid-radicles by these tests. The solution is accordingly prepared as is directed below, under *a*, *b*, *c* :—

(*a*) If alkali-metals only are present, the solution to be tested must be rendered neutral or *very faintly* alkaline. The most suitable reagents for producing this condition are dilute HNO_3 and NaOH-solution. According to the reaction of the solution, one or other of these reagents is added until the solution does not affect the colour of test-papers.

(*b*) If metals other than the alkali-metals are present, the substance must be boiled with excess of Na_2CO_3-solution, filtered, and acidified with HNO_3; the CO_2 is then boiled off and the solution is carefully neutralised with NaOH-solution.

(*c*) If metals of Group II. or III. are present, the following treatment may be requisite to ensure their removal :—

The solution is acidified, if it is not already acid, with dilute HCl, and H_2S is passed to saturation; the liquid is then filtered, and AmOH and Am_2S are added to the filtrate: the liquid is then filtered again and the filtrate is reserved. The filtrate will contain the ammonium salts of the organic acid-radicles, together with excess of Am_2S, and its further treatment will depend upon whether only Ba, Sr, Ca, Mg are present, or other metals are also present :—

If no other metals are present, acidify the liquid with dilute HCl, boil off the liberated H_2S, filter if necessary, and neutralise the filtrate with NaOH-solution. This liquid may now be tested with the reagents mentioned in pars. 1344, 1345. (See *Note* below.)

If other metals are present, acidify with dilute HCl, boil off the H_2S, add Na_2CO_3-solution in excess, filter, acidify with HNO_3, boil off CO_2, and carefully neutralise with NaOH-solution: then proceed to test the liquid by pars. 1344, 1345.

Note.—A separate solution of the original substance must be prepared for the $AgNO_3$ test (1346), in which dilute HNO_3 is used instead of HCl, else the $AgNO_3$-solution will give a white precipitate of AgCl which may be mistaken for an organic salt.

The results given by the tests in pars. 1344–1346 are not pronounced, and are in some cases not even visible, if the reagents are added to very dilute solutions, and strong solutions should therefore always be employed.

It will be seen that the results which are yielded by other substances besides the organic acid-radicles are given in paragraph 1344.

1344. ACTION OF $FeCl_3$-SOLUTION ON NEUTRAL SOLUTION OF ORGANIC SUBSTANCES.

Result.	Observation.	Inference.
a. A red coloration is produced in the cold.	The coloration is destroyed by $HgCl_2$-solution, and is unaltered by dilute HCl.	Thiocyanate.
	The coloration is destroyed by dilute HCl; a red precipitate forms on boiling.	Formate, or acetate.
	(Diff.) In the original solution $AgNO_3$ gives a black precipitate in hot solution.	Formate.
	(Diff.) Strong H_2SO_4 gives a smell of HĀ.	Acetate.
	The coloration is with difficulty destroyed by HCl. $CaCl_2$ produces a white precipitate in the original solution on boiling. (Diff. from formate and acetate.)	Meconate.
	The coloration is destroyed by HĀ, but not by HCl.	Pyrogallol.
b. A purple coloration is produced in the cold.	The purple colour is not destroyed by HĀ. A salicylate when heated with strong H_2SO_4 and CH_3OH gives off methyl salicylate. (Diff. from phenol.)	Salicylate.
	The purple colour is destroyed by HĀ. Phenol solution when treated with AmOH and bleaching-powder turns blue. (Diff. from a salicylate.)	Phenol.
c. A blue-black precipitate is produced in the cold.	The precipitate disappears on boiling. With a gallate KCN produces a red coloration. (Diff. from a tannate.)	Gallate.
	The precipitate is permanent on heating. Ammoniacal $CuSO_4$-solution produces a green precipitate with a tannate. (Diff. from a gallate.)	Tannate.
d. A blue precipitate is produced in the cold.	The colour of the precipitate is changed by KOH into brown.	Ferrocyanide.
e. A buff or reddish precipitate is produced in the cold.	The addition of HCl gives crystalline scales of benzoic acid. The original substance burns with a smoky flame. (Diff. from a succinate.)	Benzoate.
	The precipitate is soluble in HCl. A succinate is precipitated on the addition of $BaCl_2$, AmOH, and alcohol. (Diff. from benzoate.)	Succinate.
	On the addition of HCl hippuric acid separates. The original substance burns with a smoky flame, and evolves NH_3 and C_6H_6 when it is heated with soda-lime.	Hippurate.
	The reddish precipitate dissolves in HCl. Confirm by adding to the original substance $K_2Cr_2O_7$ and H_2SO_4, a blue coloration appears.	Aniline.
f. A coloration is produced in the cold.	Brown or olive-green coloration. Confirm by adding $FeSO_4$-solution to the original substance, a blue precipitate forms.	Ferricyanide.
	The coloration is blue.	Morphine.
g. No effect is produced until the mixture is heated.	The solution reddens on being heated and forms a red precipitate.	Many alkaloids and organic bases.

1345. ACTION OF $CaCl_2$-SOLUTION ON NEUTRAL SOLUTION OF ORGANIC SALTS.

Result.	Observation.	Inference.
a. A white precipitate forms in the cold.	The precipitate is insoluble in HĀ and in KOH; when dried and heated, it scarcely chars and leaves a carbonate.	Oxalate.
	The precipitate is soluble in HĀ and in KOH; it often only appears on shaking, and chars when dried and heated. Confirm by heating the original solution with ammoniacal $AgNO_3$ (759, *Note*).	Tartrate.
	Add $PbĀ_2$ to the original solution, a white precipitate forms.	Meconate.
	The precipitate is decomposed by HCl, with separation of uric acid.	Urate.
	The precipitate is unchanged when heated.	Hippurate, benzoate, or tannate.
b. A white precipitate forms on heating.	The precipitate is soluble in HĀ and insoluble in cold KOH; it chars on being dried and heated.	Citrate.
	The precipitate forms more readily in the presence of alcohol; it chars on being heated. Confirm by adding $PbĀ_2$ to the neutral solution, and fusing the precipitate under water (753).	Malate.
c. A white precipitate forms in the presence of alcohol.	Confirm by adding to the neutral solution $FeCl_3$, a reddish precipitate forms.	Succinate.

1346. ACTION OF $AgNO_3$-SOLUTION ON NEUTRAL SOLUTION OF ORGANIC SALTS.

Result.	Observation.	Inference.
a. A white precipitate forms in the cold.	The precipitate is unaltered when heated.	Oxalate, meconate, salicylate, malate, or hippurate.
	The precipitate dissolves when heated: it is not formed in dilute solution.	Acetate.
	The precipitate forms in strong solutions, rapidly turning black; in dilute solutions a black precipitate of Ag is formed when the liquid is heated.	Formate.
	The precipitate turns grey when it is heated.	Citrate, or malate.
	The precipitate slightly darkens when it is heated.	Succinate, or benzoate.
	The precipitate rapidly turns black.	Tannate, gallate, urate, phenol, and hydroquinone.
	The precipitate turns black when the liquid is boiled.	Tartrate.
	The precipitate is soluble in AmOH, and insoluble in dilute HNO_3.	Cyanide or thiocyanate.
	The precipitate is insoluble in AmOH, and insoluble in dilute HNO_3.	Ferrocyanide.
	White curdy precipitate. soluble in NH_4OH and in HNO_3.	Cyanate.
	Immediate black precipitate.	Pyrogallol.
b. An orange precipitate is formed.	The precipitate is soluble in AmOH, and insoluble in dilute HNO_3.	Ferricyanide.

EXAMPLE SHOWING HOW TO ENTER THE RESULTS OF ANALYSIS OF A COMPLEX SUBSTANCE.

1347. The substance given for analysis consisted of a powder containing pink, blue, white, and black particles. It smelt faintly of ammonia.

PRELIMINARY EXAMINATION FOR METALS.

Experiment.	Observation.	Inference.
EXPT. I.—Heated in a small dry test-tube.	Water given off which turned turmeric-paper brown.	Pres. of H_2O.
		Pres. of NH_4.
	Strong smell of NH_3.	Pres. of NH_4.
	Substance blackened, no smell of burning.	Prob. pres. of Co, Cu, and abs. of $\bar{T}$ and $\bar{A}$.
	Slight white sublimate.	Pres. of As, NH_4, Hg.
Confy.—Held in the upper part of the tube a glass rod with a drop of lime-water hanging on its end.	The lime-water became milky.	CO_2 evolved.
	Brown nitrous fumes evolved, recognised by their smell.	Pres. of nitrate.
	Cl evolved, found by its smell and by bleaching litmus.	Pres. of Cl.
Confy.—Boiled a portion of the substance with KOH-solution.	NH_3 was evolved, recognised by its smell, and by giving white fumes with strong HCl.	Pres. of NH_4.
Confy.—Heated strongly another portion of the dried substance with Na_2CO_3 in a bulb-tube.	No mirror formed.	Abs. of Hg and As.
EXP. II.—Heated a portion of the substance on a loop of platinum-wire in the Bunsen-flame, moistened with HCl and heated again in the flame.	*Bright yellow* flame.	Pres. of Na.
	The flame appeared *crimson* through the indigo-prism.	Pres. of K.
	Crimson coloration, appearing *intense red* through the indigo-prism.	Pres. of Sr.
Heated for some time in the tip of the inner blowpipe-flame, moistened with HCl, and again held in the Bunsen-flame.	*Bright green* flame with *blue* core.	Pres. of Cu.

PRELIMINARY EXAMINATION FOR METALS. (*Continued*).

Experiment.	Observation.	Inference.
EXPT. III.—Heated a portion of the substance on charcoal in the inner blowpipe-flame.	The greater part of the substance fused readily, and was absorbed by the charcoal.	Pres. of a salt of K, Na.
	Deflagration occurred.	Pres of chlorate, nitrate.
	A red metallic residue remained.	Pres. of Cu.
Confy.—Fused in a clear borax-bead in the outer and inner blowpipe-flames.	In the outer flame a bead *green* whilst hot, *blue* when cold. In the inner flame *red and nearly opaque.*	Pres. of Cu.
Confy.—Fused on platinum-foil with Na_2CO_3 and KNO_3.	No *bluish green* or *yellow* mass on cooling.	Abs. of Mn and Cr.
Confy.—Fused on charcoal in the inner blowpipe-flame with Na_2CO_3.	Red metallic residue.	Pres. of Cu.
	A portion placed on a silver coin and moistened gave no black stain.	Abs. of S.

PRELIMINARY EXAMINATION FOR ACID-RADICLES.

Experiment.	Observation.	Inference.
EXPT. I.—Added dilute HCl without heating.	A colourless gas was evolved, which was free from smell, and turned a drop of lime-water milky.	Pres. of carbonate. Abs. of sulphite, hypochlorite, etc.
Heated to boiling.	Cl was evolved, recognised by its smell and by bleaching moist litmus-paper.	Pres. of nitrate, chlorate, or some other oxidising substance.
EXPT. II.—Added strong H_2SO_4.	A bright yellow chlorous gas evolved, which crackled when warmed.	Pres. of chlorate.
Confy.—Dropped in copper turnings and heated.	Reddish brown fumes evolved.	Pres. of nitrate.
Heated strongly, cooled, and rinsed out tube.	The tube when dry was seen not to be etched.	Abs. of fluoride.
Confy.—Boiled a portion of the substance with water, added strong H_2SO_4, cooled and poured in $FeSO_4$-solution carefully.	A brown ring formed on the surface of the acid.	Pres. of nitrate.

These lines run across both pages.

EXAMINATION FOR METALS

Boiled a portion of the substance with $FeCl_3$, $FeSO_4$ and KOH,

Boiled a portion of the substance with water ; as it did not completely undissolved residue : effervescence occurred, and on boiling, Cl was perceived ; the substance was completely dissolved. Cooled this soln. to give no pp. on addition of a little dilute HNO_3 :—

No pp. *Abs. of Group I.* Hg˙, Ag, and prob. Pb.	Diluted with water and passed H_2S until the liquid smelt strongly of	
	A black pp. Examd. by Table II.	*Filtrate* which gave no further pp. with H_2S Boiled until it no longer smelt of H_2S, tion of HNO_3 (*Pres. of Fe*). Warmed the some $AmHMoO_4$-solution, warmed ; no
		A brown pp. Examd. by Table III.A.

IN THE WET WAY.

added HCl in excess, no blue pp. :—*Absence of CN.*

dissolve, the sol^n. was decanted, and a little dilute HCl poured upon the smelt. Added a little strong HCl, boiled as long as any smell of Cl was and mixed it with the water sol^n. which had been proved previously

<table>
<tr><td colspan="3">the gas, filtered :—</td></tr>
<tr><td colspan="3">was pink (prob. pres. of Co).
added some strong HNO_3 and boiled to dryness : the colour of the soln. changed to light brown on addi-
residue with HCl, it dissolved completely (Abs. of Silicate). Added a small portion of the HCl soln. to
pp. : Absence of (PO_4). To the remainder added AmCl, then excess of AmOH, and boiled ; filtered :—</td></tr>
<tr><td colspan="3">Filtrate was again pink (Presence of Co) : added much Am_2S and boiled, filtered :—</td></tr>
<tr><td rowspan="2">A black pp.
Examd. by Table III.B.</td><td colspan="2">Filtrate was yellow (Absence of Ni): added Am_2CO_3, filtered :—</td></tr>
<tr><td>A white pp.
Examd. by Table IV.</td><td>Filtrate.
Examd. by Table V.</td></tr>
</table>

EXAMN. OF PP. IN GROUP II.—Removed from the filter into a porcelain dish and boiled with KOH, filtered :—

<table>
<tr><td rowspan="4">Filtrate :— Acidified with HCl, a white milky liquid only :—
Abs. of Group II.B.</td><td colspan="4">Pp. removed from filter by a glass rod into a porcelain dish and boiled with strong HNO_3 as long as any red fumes came off, added dilute H_2SO_4 and stirred well :—</td></tr>
<tr><td rowspan="3">No pp. :—
Abs. of Hg and Pb.</td><td colspan="3">Added to solution excess of AmOH : blue solution (Pres. of Cu) :</td></tr>
<tr><td rowspan="2">No. pp. :—
Abs. of Bi.</td><td colspan="2">Acidified the blue soln. with HCl and saturated with H_2S ; filtered off the black pp. rapidly and boiled it with dilute H_2SO_4 :—</td></tr>
<tr><td>Pp. : dissolved in a little boiling dilute HNO_3, added AmOH in excess, then excess of HĀ, then K_4FeCy_6, chocolate red pp. :—
Pres. of Cu.</td><td>Filtrate : diluted much and passed H_2S, no pp. :—
Abs. of Cd.</td></tr>
</table>

EXAMN. OF PP. IN GROUP III.A.

Dissolved in a little boiling dilute HCl, added pure NaOH in excess, boiled and filtered :—

<table>
<tr><td rowspan="2">Filtrate : added AmCl in excess, no pp. :—
Abs. of Al.</td><td colspan="2">Pp. : dried and fused on platinum-foil with Na_2CO_3 and KNO_3, boiled the colourless (Abs. of Cr) mass when cold with water ; decanted from the undissolved residue :—</td></tr>
<tr><td>Residue in the dish, dissolved by boiling with a little HCl, added several drops of KCNS : a blood-red coloration :—
Pres. of Fe.</td><td>Soln. being colourless indicated abs. of Cr.
Acidified with HĀ, boiled, and added $Pb\bar{A}_2$, no yellow pp. :—
Abs. of Cr.</td></tr>
</table>

EXAMN. OF PP. IN GROUP III.B.

Rinsed the pp. off the filter with some cold dilute HCl, stirred well and filtered :—

<table>
<tr><td rowspan="2">Pp. was black and had already been proved to contain no Ni ; fused a portion into a clear borax bead : bead blue in both flames :—
Pres. of Co.</td><td colspan="2">Filtrate : boiled until it no longer smelt of H_2S, added a crystal of $KClO_3$, boiled until the smell of Cl ceased, cooled and added pure NaOH in excess :—</td></tr>
<tr><td>No pp. :—
Abs. of Mn.</td><td>Passed H_2S into the soln. no pp. :—
Abs. of Zn.</td></tr>
</table>

pp. in a few drops of HCl upon a watch-glass, dipped a loop of Pt-wire into the sol$^{n.}$ and held it in the Bunsen-flame : a crimson colour was imparted to the flame, which appeared intense red through the indigo-prism : *Pres. of Sr.*

This coloration was followed by a yellowish green very persistent col$^{n.}$: *Pres. of Ba.* Confirmed by spectroscope.

2. *Exam$^{n.}$ in the Wet way.* Dissolved the rest of the pp. in as little boiling $H\bar{A}$ as possible ; to a small part of the solution, when perfectly cold, added $CaSO_4$-sol$^{n.}$, an immediate pp. formed : *Pres. of Ba.*

To the remainder of the $H\bar{A}$-sol$^{n.}$, proved to be acid to litmus, added K_2CrO_4 until the liquid appeared yellow, warmed and poured through a double filter :—

<table>
<tr><td rowspan="2">Pp., which contained all the Ba present, was rejected.</td><td colspan="2">To the clear filtrate, which was orange-red in colour, added AmOH until the colour changed to light yellow, then added Am_2CO_3 in excess and filtered :—</td></tr>
<tr><td>Filtrate was rejected.</td><td>Pp.: dissolved in as little boiling $H\bar{A}$ as possible ; added to a small portion of the sol$^{n.}$ $CaSO_4$-sol$^{n.}$ and boiled : a pp. formed :—
Pres. of Sr.
To the remainder of the $H\bar{A}$-solution added H_2SO_4, boiled, filtered, and to the filtrate, which gave no pp. after being boiled with more H_2SO_4, added AmOH in excess and $Am_2C_2O_4$: no pp. :—
Abs. of Ca.</td></tr>
</table>

EXAM$^{N.}$ OF FILTRATE FROM GENERAL TABLE FOR GROUP V.

Evaporated the filtrate to dryness in a porcelain dish, scraped out the residue upon platinum-foil, and ignited strongly until white fumes ceased to appear : dissolved the residue off the foil by boiling with water to which several drops of HCl had been added, divided the sol$^{n.}$ into two unequal parts :—

<table>
<tr><td>To the larger portion added several drops of H_2SO_4 and boiled, then AmOH in excess and several drops of $Am_2C_2O_4$; on heating, a slight pp. formed ; filtered, and added to the clear filtrate Na_2HPO_4, a white crystalline pp. :—
Pres. of Mg.</td><td>Into the smaller portion dipped a loop of platinum wire, and held it in the Bunsen-flame, an intense yellow col$^{n.}$:—
Pres. of Na,
appearing crimson through the indigo-prism :—
Pres. of K.
Confirmed the pres. of K by stirring a fresh portion of the sol$^{n.}$ with H_2PtCl_6 on a watch-glass, a yellow pp. formed.</td></tr>
</table>

Metals found :—Cu, Fe, Co, Ba, Sr, Mg, Na, K, NH_4.

EXAM^N. FOR ACID-RADICLES.

The following acid-radicles have already been detected: (CO_3), (NO_3), (ClO_3).

By reference to the Table of Solubility (1266), under the columns corresponding to the above metals, the only salt insoluble in acids is found to be $BaSO_4$; since Ba is present, and the substance is entirely soluble in acids, *(SO_4) is absent.*

The following acid-radicles have also been proved to be absent in the general examination for metals:—

(CrO_4), by the HCl-solution not becoming green on passing H_2S.

(AsO_3) and (AsO_4), by no pp. forming in Group II.B.

(SiO_3) and (SiF_6), by no residue insol. in HCl remaining on evaporating to dryness with HCl for Group III.A.

(PO_4), by testing with $AmHMoO_4$ in the HCl sol^n. for Group III.A.

The organic acid-radicles ($\bar{A}$) and ($\bar{T}$) are absent, since there was no smell of burning on heating the substance.

The only commonly occurring acid-radicles remaining to be specially tested for are therefore Cl, Br, I, (C_2O_4), and (BO_3); and of these Br and I are probably absent, since no violet fumes of I or brown fumes of Br were evolved with strong H_2SO_4.

Boiled a portion of the substance with pure Na_2CO_3-sol^n. and filtered; acidified portions of the filtrate with—

HNO_3	$H\bar{A}$
Added $AgNO_3$, a perfectly white pp., easily sol. in AmOH:— *Pres. of Chloride.*	*Added $CaSO_4$*, no pp.:— *Abs. of (C_2O_4).*

Moistened a piece of turmeric-paper with the HCl-sol^n. of the substance and dried it at 100°: no reddish-brown stain was produced:—*Abs. of (BO_3).*

Acid-radicles found:—CO_3, NO_3, ClO_3, Cl.

Found { *Metallic-radicles*: Cu, Fe, Co, Ba, Sr, Mg, Na, K, NH_4.
Acid-radicles: CO_3, NO_3, ClO_3, Cl.
Combined H_2O

PART IV

SECTION VIII

THE LABORATORY AND ITS FITTINGS ; APPARATUS, CHEMICALS, AND REAGENTS

In Part IV directions are given which have been found by experience to be of value in fitting and furnishing a laboratory and in maintaining it in working order.

THE LABORATORY BUILDING, AND ITS FITTINGS.

1360. The methods of building, fitting, heating, and ventilating a Chemical Laboratory are of prime importance in securing the comfort, health, and convenience of the laboratory students.

The suggestions given in the following paragraphs are by no means exhaustive and they apply mainly to the preparation of a chemical laboratory for analytical purposes.

It is evident that the details of furnishing and fitting must be influenced by the size, purpose and position of the laboratory. Provision must be made for the adequate lighting of the working-benches, for draught, waste and drainage ; and these matters should be carefully planned before the laboratory building is erected, since much trouble and inconvenience may be caused by first building the laboratory and afterwards endeavouring to adapt the general fittings to an unsuitably designed structure.

The Building should provide for adequate air space and ventilation. The window-lighting should be from both the top and the sides of the room, and on as ample a scale as possible.

The inner surface of the walls should either be of white glazed brick, which can be easily cleansed when necessary, or the brick or plaster surface should be covered with *white* lime-wash or distemper, which can be frequently and cheaply renewed. The windows should be glazed with *colourless* glass. This absence of colour in the walls and windows is necessary to enable the accurate judgment of colours to be made which is necessary to the analyst.

1361. **Draught Arrangements.**—The means of producing a draught for the removal of acid vapours and fumes from the chemical laboratory must be ample, and this is best secured by means of

an electric fan. As a rule stoneware draught-flues are preferable to those made of zinc or lead. These draught arrangements may be made to aid in the ventilation of the laboratory as well as to serve for efficiently exhausting the draught-chambers and bench flues.

Draught Chambers.—Around the walls, in the spaces between the windows, there should be large and small recesses, each of which is lined with white glazed tiles, has a glazed hood above, and is closed with a sliding sash in front; it should be provided with two outlets, one at the top and the other near the bottom, through which a strong draught is produced by the fan.

These draught-chambers should be provided with several gas-supplies for Bunsen-burners, the taps being on the outside of the chamber; they should also be provided with means for lighting the interior. The bottom of the chamber may be covered with sheet-lead, and should have a small grid through which liquids escape into the waste. Some at least of these chambers should also be provided with a water-supply pipe.

A strip of rubber or fibre draught-excluder fixed along the top of the inner frame and lightly touching the glass prevents the escape of fumes when the sash is partly opened.

One or more of the draught-chambers should be reserved for the hydrogen sulphide apparatus (1371).

It will be found well to provide this H_2S-chamber with small doors, which are only opened when the gas is to be used: this prevents the gas from escaping in large quantity into the laboratory, as it would do if the large sash were thrown up for each operation. A frame containing pairs of little hinged glazed doors, each about six inches by eight, may be introduced beneath the sliding sash. The arrangement enables a student to open as much of the chamber-front as is necessary for passing the gas through a solution: while the whole sash can be raised for cleansing or replenishing the hydrogen sulphide apparatus.

One of the draught recesses is kept open for the steam-ovens, and the small boiler and condenser which are described in paragraph 1377.

1362. Drainage and Waste.—It is essential that the waste-service should be adequate. Lead *pipes* are unsuitable for this purpose, since they are liable to be corroded by acids, and are difficult to repair and to clear if they should become obstructed. The open trough system, made of stoneware, or of wood lined with sheet lead protected by a coating of bitumen, is to be preferred; the drainage from the benches and draught-chambers should also be made readily accessible. The main troughs should be taken

the drain may be readily examined and cleared by the removal of suitably arranged floor-boards.

Washing Sinks.—Two or more deep stoneware-sinks should be provided for general use, and should have large water-taps fixed above them at some distance from the back of the sink.

It will be found convenient if each sink is supplied with three taps. Two of these deliver hot and cold low-pressure water; and a third is connected with a high-pressure water service, upon which a fire-hose can be at once adapted. A stout wooden board pierced with small holes may be laid upon the bottom of the sink to serve as a strainer and to prevent solid fragments from getting into the outflow pipe; the soft wooden surface also tends to prevent the breakage of glass or porcelain vessels.

Note.—Lead-covered sinks lessen the risk of breakage arising from the dropping of apparatus while it is being washed, but they are easily corroded by acids and are less cleanly than stoneware. The wooden grid already mentioned, which is laid on the bottom of a stoneware sink, is a very efficient and permanent grid, and saves breakages.

1363. **Working Benches.**—In Fig. 66 facing page 331 a block of four laboratory benches is shown. Two of these are presented to the observer, and are therefore visible in detail. The arrangement of four benches in one block is convenient, since it enables the washing-sinks and the water-taps to be placed at the end of each bench and yet to be accessible to each student. The surface of the bench is thus prevented from being wetted and soiled when apparatus is washed.

The Bench Sinks may be of stoneware, with perforated movable wooden false bottoms, which prevent breakage and serve as grids (*Note*, 1362). Half-inch outlet pipes unprotected by metal grids discharge into stoneware pots, the overflow from which into the drain-pipes is through a curved stoneware tube near the top. Any fine solid matter, which passes down the sink-pipe, settles in this trap-pot, and is got rid of by taking out the pot and emptying it into a pail at frequent intervals.

Any stoppage in the straight sink-pipe is readily pushed through with a stout cane. Over each sink there are three low-pressure water-taps for washing and for supplying condensers, and two high-pressure water-taps for aspirators.

A Stoneware Pocket is hung upon the end of each working bench to receive waste filter-papers, broken glass, and other solid refuse. This pocket is frequently emptied.

Bench Draughts.—Each bench is provided with an aperture leading to a strong draught, and into this aperture a light copper or porcelain hood can be fitted, which serves to carry away acid

vapours or badly-smelling gases. The aperture is closed with a wooden plug when the hood is not in use, so as not to diminish the draught on other benches.

The copper hoods are occasionally cleansed and painted with Japan-black, in order to protect them against corrosion by acid fumes : fixed light earthenware hoods are fragile, but present the advantage of not being corroded by acids. A glazed draught-hood extending along the top of the centre shelf-rack of the bench has been found to be satisfactory : all heating and evaporation of liquids is then carried out on a raised shelf under this hood.

The Laboratory Bench may be made of stout teak or of American walnut, the wood of the front being stopped and varnished, and the working surface of the bench being saturated with oil and then well rubbed. The working surface is preserved by being occasionally thoroughly washed, dried, and rubbed down with a mixture of equal measures of boiled linseed oil and turpentine.

The bench may be 3 feet in height with a depth of 25 inches, and a space of 7 inches between the reagent-shelves above the bench will be found suitable for ordinary bottles. A gangway at least six feet in width should be provided between the rows of benches, and beneath this gangway the main drainage-troughs should run.

Two gas-taps are fixed on each bench for supplying Bunsen-burners. If gas is not available, Bunsen-burners for consuming methylated spirit or petroleum (1366) may be used with advantage. One electric glow-lamp or gas-burner is provided at a convenient height for illuminating the bench at night. If gas is used an incandescent mantle gas-burner is most suitable for this purpose since it gives the nearest approach to white light.

Bench Lockers.—Each working-bench is supplied with two lockers, and each locker has two drawers above it. In order to lessen the number of locks, which are liable to rust in the laboratory atmosphere, a flat iron bar which swings on a pin is fastened upon a staple by a padlock in front of the two drawers and locker. By this arrangement of lockers two students are enabled to use the same bench at different times.

Each locker should have a different key, but all the locks should be under the control of master-keys kept by the attendant and the teachers. The drawers should be about $3\frac{1}{2}$ inches in depth, and may be suitably divided by wooden strips. A shelf in the locker should not extend more than half across, so as to leave standing room for tall apparatus.

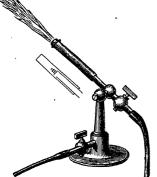
1364. Preparation and Combustion Benches. Besides the ordinary working-benches, there should be at least one long bench,

well supplied with gas and water-taps and with overflow-pipes. This bench serves for making up solutions, for distillations and for other large operations.

There should also be a long bench made of slate, and covered at a height of several feet with a metal hood, under which is a good draught-outlet. This bench must be supplied with a half-inch gas-pipe and taps, and with water-taps and waste-overflows : it serves to support water-baths, air-baths, combustion-furnaces, and gas furnaces of all kinds.

1365. Blowpipe-table and Blowpipes.—A table with a raised edge, and covered with sheet lead or zinc, is furnished with gas-taps to supply standing gas-blowpipes, and luminous-burners for bending glass, and two or more Fletcher-bellows should stand beneath it. It is also well to have an electric blower near at hand to supply an air-blast to the blowpipes for lengthened heating operations.

The Fletcher Bunsen-blowpipe (Fig. 10, 12) will naturally find its place on this table. It is also well to keep a Bunsen gas-blowpipe (Fig. 67) on the table for more elaborate glass-blowing, and

FIG. 67. FIG. 68.

BUNSEN GAS-BLOWPIPE.

HERAPATH GAS-BLOWPIPE.

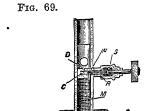
a Herapath-blowpipe (Fig. 68) for smaller heating operations. The upper part of the Herapath-blowpipe can also be purchased without the foot, and this can be fitted into a Bunsen-burner and used on the working-bench.

1366. Spirit and Petroleum Burners and Blowpipes.—Heating and blowpipe-work must occasionally be done without a supply of coal-gas and without an air-blast. Recourse may then

be had to the Bunsen-burners and blowpipes which burn the vapour of methylated spirit or petroleum (Figs. 69, 70, 71).

FIG. 69.

SPIRIT-VAPOUR BUNSEN.

FIG. 70.

PETROLEUM-VAPOUR BUNSEN.

In these forms of apparatus the burner is first heated by burning some methylated spirit in a circular gallery surrounding the burner, and the supply of liquid coming into the base of the burner is then vaporised by contact with the hot burner.

FIG. 71.

BENZOLINE BLAST-LAMP.

In the case of the spirit-vapour Bunsen (Fig. 69) the liquid is supplied to the burner by gravitation from a vessel at higher level.

In the petroleum-Bunsen (Fig. 70) the petroleum is raised by the pressure of air which is forced by a little pump, shown on the right of the figure, into the upper part of the reservoir.

The blast of the blowpipe-lamp (Fig. 71) is maintained by the pressure of the vaporised liquid inside the reservoir.

1367. **Chemical Store-room and Balance-room.**—Opening into the general laboratory there should be five rooms, since it is usual to arrange a separate room for each of the following purposes—

(1) Balances.
(2) Chemical stores.
(3) Gas and water analysis.
(4) Physical apparatus.
(5) Reference library and writing.

If space is limited, and only two rooms can be provided, one of the two is fitted with shelves for stores of chemicals and

apparatus. The other may be used as a reference-library : also for delicate metal apparatus, such as chemical balances, microscopes, spectroscopes, and polariscopes.

The balances and delicate apparatus should stand on a broad shelf which is at a convenient height for sitting, the shelf being supported on iron brackets from the wall so as to secure the chemical balances against disturbance from the vibrations of the floor. The spectroscope and polariscope should have draw-curtains of black lining material, so arranged that light from outside may be excluded when the instruments are in use.

A large central table should be provided in this room for use in writing and reading.

A low table with a raised edge is also necessary for gas-analysis apparatus and for other experiments involving the use of mercury ; and in order to provide against the loss of mercury spilt from the table, it will be well to cover the floor with linoleum with turned-up edges.

BENCH-APPARATUS.

Detailed descriptions of this apparatus may be obtained from the illustrated and descriptive price lists furnished by apparatus-sellers.

1368. A list of the apparatus which should be kept in each bench-locker will be found preceding page 1. The separate items of that list are repeated here, with the addition of details of dimensions and of other useful information.

In Part I. of the book, directions are given for preparing and fitting this apparatus, and the paragraph numbers in the lists below refer to these descriptions.

The Bunsen-burner with its rubber tube may be left attached to the gas-tap on the bench ; all the other apparatus should be locked up in the bench-locker when it is not in use. Most of this apparatus is seen on the bench in Fig. 66, facing page 331.

The approximate decimal and English equivalents of length and capacity are given to save reference or calculation.

1 Bunsen-burner (2), about 5½ inches (14 cm.) in height, with ⅜-inch (1 cm.) tube, and with means of closing the air-holes.
1 Rose-top to fit the burner (2).
1 Fletcher's Argand-Bunsen burner (3), ¾-inch (1·8 cm.) size, is convenient for boiling the wash-bottle, but is not essential.
1 Piece of red or black rubber tubing, $\frac{5}{16}$-inch (7·5 mm.) in internal diameter and 20 inches (50 cm.) long, to supply gas to the burner.
1 Test-tube stand with twelve holes, two of which are at least 1 inch (2·5 cm.) across ; best without draining-pegs.
1 Test-tube brush (19).
12 Test-tubes, 5 inches (12·5 cm.) long, ⅝-inch (1·5 cm.) in internal diameter.

2 Boiling-tubes, 6 inches (15 cm.) long, 1 inch (2·5 cm.) in internal diameter.
2 Round glass plates, ground on one side, 3 inches (7.5 cm.) across.
2 Porcelain evaporating-dishes with spouts, glazed inside and out, and 3 inches (7·5 cm.) in diameter.
2 Watch-glasses, 2 inches (5 cm.) across.
1 Conical flask (Fig. 21.B., 36) of 4 ounces (120 c.c.) capacity.
1 Wedgwood-mortar, 4 inches (10 cm.) across, and pestle with wooden handle.
1 Galvanised iron tripod-stand, 7 inches (17·5 cm.) in height, with round top 4 inches (10 cm.) across (Fig. 21.B., 36); these dimensions are suitable to the above Bunsen-burner.
1 Square of coarse iron wire-gauze, 5 inches (12·5 cm.) in the side (Fig. 21.B., 36); best with the corners clipped off.
(A square of asbestos millboard may be used instead of the gauze.)
3 Plain glass funnels (Fig. 31, 43), two of them $2\frac{1}{2}$ inches (6·5 cm.) across, and one 2 inches (5 cm.) across.
3 Beakers without lips, wide form, of 3, 4 and 6 oz. (100, 120 and 200 c.c.) capacity.
3 Glass rods, round at the ends, 7, 6, and 3 inches (17·5, 15 and 7·5 cm.) in length (15).
1 Piece of platinum foil, 1 inch square (2·5 cm. square).
2 Pieces of mounted platinum wire (14), each 2 inches (5 cm.) long and about as stout as an ordinary sewing needle.
1 Blowpipe, Black's japanned tin (Fig. 9, 11).
1 Pipe-clay triangle, 2 inches (5 cm.) along its side (Fig. 65, 1308).
1 Wash-bottle (17), made by fitting a conical 18-ounce (500 c.c.) flask, which is at least 1 inch (2·5 cm.) across the inside of the neck.
1 Wooden filter-stand (Fig. 33, 43), rod 12 inches (30 cm.) high, two rings on one boss, each $2\frac{1}{4}$ inches (5·5 cm.) across, foot 5 by 8 inches by $\frac{1}{2}$ inch (12·5 by 20 by 1·3 cm.).
1 Pair of polished brass crucible-tongs, 6 inches (15 cm.) long.
1 Small horn spatula, $3\frac{1}{2}$ inches (9 cm.) long.
1 Wicker oval draining-basket, 10 inches by 8, and 4 inches deep.
Cut filter-papers, $4\frac{1}{2}$, $3\frac{1}{2}$, and $2\frac{3}{4}$ inches (11·5, 9 and 7 cm.) across.

APPARATUS FOR GENERAL USE IN ANALYSIS.

1369. **The Following Apparatus** should be kept in the laboratory for the general use of students who are doing chemical analysis.

One set will suffice for about twelve students. Each article should have its own place in the laboratory, and should be replaced immediately after use, since it may be required by other students.

3 Nests of three or four of the smallest brass cork-borers.
6 Triangular files without wooden handles.
3 Thin round files without wooden handles.
Several lengths and pieces of hard glass tubing, about $\frac{1}{8}$ inch (3 mm.) internal diameter.
Ignition-tubes, 3 inches long by $\frac{1}{4}$ inch across (7·5 by 0·6 cm.).
Corks as free as possible from holes and cracks, sizes varying from $\frac{3}{8}$ to $\frac{3}{4}$ inch across (1 cm. to 2 cm.).

Several retort-stands of galvanised iron (Fig. 34, 44), upright rod 16 inches (40 cm.), foot 6 by 3½ inches (15 by 9 cm.) with three brass or gun-metal rings, diminishing from 3 inches (7·5 cm.) across, and metal clamp (Fig. 22, 35).
3 Tubulated retorts of 6 ounces (200 c.c.) capacity.
6 Thistle-funnels, of assorted length.
6 Clock-glasses, about 4 inches (10 cm.) across.
Pieces of red or black rubber tubing, $\frac{3}{16}$ inch (5 mm.) in internal diameter and 1½ inches (4 cm.) long.
A good supply of wooden spills, or thin strips of wood.
A good supply of wax tapers, about 11 inches (27 cm.) long.
1 Spirit-lamp, 4 ounces (120 c.c.) in capacity, with earthenware wick-holder and ground-glass cap (5).
1 Charcoal borer of conical form.
4 Tin filter-dryers (Fig. 39, 48).
4 Porcelain crucibles, 1½ inches (4 cm.) across, with covers.
1 Iron mortar, 8 inches (20 cm.) across, with pestle.
1 Fletcher's No. 5 foot-bellows (Fig. 11, 12), and a blowpipe-table covered with sheet zinc or lead.
1 Fletcher's Bunsen-burner blowpipe, with central blast, and two taps (Fig. 10, 12).
1 Bunsen-blowpipe, and one Herapath-blowpipe (1365).
1 Fletcher's solid-flame burner, with tripod for large dishes (Fig. 2, 3).
1 Fletcher's injector-furnace for strongly heating large crucibles.
1 Microscope, with at least a ¼-inch (6 mm.) object glass.
1 Spectroscope, Bunsen's table form (65).
1 Spectroscope, direct vision, pocket form (64).
1 Indigo-prism, stoppered, and filled as is described below :—

Clear indigo-solution is made by mixing commercial sulphindigotic acid with about ten times its measure of strong sulphuric acid, and letting this settle for several days.

The prism is nearly filled with this solution of indigo ; the dry stopper is inserted into the dry neck and is securely fastened down with fine copper wire; melted paraffin wax is then allowed to flow over the junction of the clean dry stopper and neck, and to harden over it.

1 Agate mortar 3 inches (7·5 cm.) across, and pestle.

This mortar is used for reducing hard substances to fine powder, after they have been already broken into minute fragments. The process of powdering in the agate mortar must be effected by trituration, since if blows are struck with the pestle the mortar may be broken.

2 Small leaden cups, about 1½ inches (4 cm.) across and ¾ inch (2 cm.) deep (654). These are made by beating sheet-lead into shape.
2 Copper water-baths, 5 inches (12·5 cm.) across, and with four diminishing rings (Fig. 27, 38).

One large bath with several openings (Fig. 28, 38) may with advantage replace these smaller baths. The baths should be about two-thirds filled with water, and the flame should be so adjusted that the water is kept just boiling. Evaporating basins placed on the bath cannot be heated above 100° C.

2 Pairs of conical flasks, fitted as is shown in Fig. 53 (176).
2 Tubulated flasks, 4 ounces (120 c.c.) in capacity (Fig. 56, 474).
2 Clarke's retorts with condensers (Fig. 57, 542).

A box of assorted pieces of wood charcoal, as free as possible from cracks and from bark.

HYDROGEN SULPHIDE APPARATUS.

1370. **Hydrogen sulphide Gas** is constantly required by the analyst, and should be readily obtainable at any time in a constant stream; but arrangements must be made for preventing this poisonous and badly-smelling gas from polluting the atmosphere of the laboratory. These objects, together with economy of materials, are better secured by the use of a large apparatus in common by many students than by the employment of a small private apparatus by each student.

The gas is most readily obtained by the action of somewhat diluted cold commercial hydrochloric acid upon fragments of ferrous sulphide.

1371. **General Hydrogen sulphide Apparatus.**—The apparatus in which the gas is prepared has assumed many forms. The Kipp-apparatus (Fig. 73, 1272) is probably in most general use, but the apparatus shown in section in Fig. 72 and described below is also recommended by its simplicity, efficiency, and cheapness.

Two large tubulated bottles, A and B, of at least 2 quarts ($2\frac{1}{2}$ litres) capacity each, are fitted as is shown in the figure. The tubulures of the bottles are connected together by a piece of broad rubber tubing, and the bottle B is also connected with the wash-bottle C by narrow rubber tubing. Rubber stoppers should be used, since they are more durable and gas-tight than ordinary corks. The delivery tube D is connected with the doubly-bent tube from the washing-bottle by means of a rubber joint, which can be partially or entirely closed by means of a screw-clamp E.

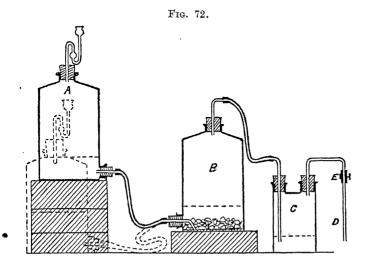
In charging the apparatus, the bottle B is laid on its side and is then filled with lumps of ferrous sulphide, which should be free from powder, since the powder is apt to choke the rubber connecting-tube, and to continually generate gas in B when the production should be arrested. The washing-bottle C is then partly filled with water, and the three bottles are connected. The clamp E is now closed, and the bottle A is about half filled with a mixture in equal measures of strong commercial hydrochloric acid and water.

When the gas is required, the bottle A is raised upon a suitable stand, and the clamp E is gradually opened until a regular stream of bubbles passes through the water in C.

A part of the acid will flow from the bottle A into the bottle B, and will cause hydrogen sulphide to be evolved from the ferrous sulphide; and the gas will be forced out of B by the pressure of the acid which remains in A. Before it escapes through the tube D, the gas is freed from small drops of liquid, containing HCl and

$FeCl_2$, by passing through the water in C. The levels of the liquids in the bottles A, B and C, while the gas is being produced, are shown by the horizontal dotted lines.

When the gas is no longer required, the screw-clamp at E is

FIG. 72.

LARGE HYDROGEN SULPHIDE APPARATUS.

gradually tightened until the stream of bubbles through the water in C is arrested. The gas then accumulates in B, and forces the acid out of B back into A. If the glass tube at the bottom of B is bent, as is shown in the figure, the acid will be almost completely expelled. This will cause the production of the gas to cease, unless FeS-powder rests on the bottom of the bottle B. The evolution of gas will recommence, however, as soon as the clamp E is opened.

During the hours of laboratory work A should remain raised on its stand, and the apparatus will then always be ready for use. At other times A should be lowered into the position represented in dotted outline in the figure. B should be permanently somewhat raised in order to facilitate the outflow of the acid when A is lowered.

The escape of the hydrogen sulphide gas from solution in the acid is much lessened in amount if a funnel containing water or glycerine is fitted into the stopper at the top of A, or if a loosely-fitting glass stopper is dropped into the neck of the bottle.

When the acid is spent and no longer causes evolution of gas from the FeS, it is poured away and replaced by fresh acid. Lumps of FeS are also occasionally placed in B, as the substance becomes dissolved.

FIG. 73.

THE KIPP APPARATUS.

1372. The Kipp-apparatus (Fig. 73) may also be used for generating hydrogen sulphide. It is similar in its action to the one already described, but the acid vessel (*f*) is placed above the generating vessel (*c*), and the two are connected together rigidly when the apparatus is fitted up for use.

In charging this apparatus the tube of the upper vessel (*f*) is withdrawn from the ground neck of the middle vessel (*c*), and lumps of FeS are introduced into *c* through the opening while the apparatus is laid upon its side. The dry clean neck is then greased, and the tube of (*f*) fitted into the neck while the apparatus is still lying on its side. The apparatus is then placed erect, the bottom vessel (*a*) is stoppered, and the delivery-tube with closed stop-cock is fitted in at (*d*). The diluted HCl is now poured in through the neck of (*f*), and the diffusion of H_2S from the acid checked by fitting in a water-valve as shown. When the acid is spent it is withdrawn by removing the stopper in the bottom vessel (*a*).

The hydrogen sulphide apparatus should stand in a draught-chamber, which is lined with glazed white tiles and is furnished with a good draught. The bottom of the chamber should be covered with sheet-lead, furnished with a grid and drain-pipe for the outflow of the very foully-smelling spent acid, or this liquid may be poured away outside the laboratory building. The chamber must not be used for other purposes, and must be suitably lighted at night.

A large sash or door must be opened when the spent acid is poured away and the apparatus is recharged within the chamber; but a small door only should be used for introducing the solutions through which the gas has to be passed. If the front of the chamber is opened by means of a glazed sliding-sash, a frame containing pairs of glazed hinged doors, each about six inches by eight, may be introduced into the grooves beneath the sash. These doors enable the apparatus to be used with the least possible opening of the closet.

Such an apparatus should serve for the use of twelve or more students, according to the character of the work which is being done.

1373. **An Apparatus for Private Use** may be fitted as is shown in Fig. 74. The larger bottle contains pieces of ferrous sulphide, upon which HCl, diluted with an equal measure of water, is poured through the thistle-funnel. The gas passes through a little water in the smaller bottle, and thence into the solution to be saturated. The use of a small apparatus by each student in a large laboratory is not to be recommended, since it causes unnecessary waste of time and materials, and does not admit of satisfactory control.

1374. **Passing Hydrogen sulphide.**—Each student should keep a glass tube D (Figs. 72, 73, 74), which may be fitted upon the hydrogen sulphide apparatus in order to conduct the gas into a solution.

FIG. 74.

SMALL HYDROGEN SULPHIDE APPARATUS.

When a liquid is to be saturated with gas, the end of this tube should be passed down *to the bottom* of the vessel which contains the liquid. A regular stream of gas is then caused to bubble through the liquid by gradually opening the clamp E (Fig. 72), or the stopcock *d* (Fig. 73) of the larger apparatus, or by introducing a sufficient quantity of acid into the larger bottle of the small apparatus (Fig. 74).

In order to avoid unnecessary waste of gas, the liquid should be of sufficient depth to absorb much of the gas, and the bubbles should not pass too fast to be readily counted.

The passage of the gas should be continued for four or five minutes if the quantity of metal to be precipitated is large, and the liquid must smell strongly of the gas after the liquid has been shaken, and the air above it has been blown out. The tube D must be thoroughly cleansed immediately after use.

Liquid Hydrogen sulphide can often be purchased in metal bottles. When the valve of the bottle is slightly opened, a stream of the pure gas will escape. A store of ready-made hydrogen sulphide may be kept in this form, and the trouble of maintaining the apparatus for preparing the gas may thus be obviated.

1375. **Hydrogen sulphide Solution.**—It will be found convenient to keep a bottle of distilled water saturated with hydrogen sulphide. This solution is prepared by passing a stream of the gas through water which nearly fills the bottle (Fig. 81, 1395). On removing the bottle, closing its mouth tightly with the thumb and shaking its contents violently, no suction must be felt on the thumb, but a slight outward pressure: this proves that the water is saturated with the gas.

DISTILLATION OF WATER.

1376. As has been already stated (31), water ordinarily contains certain solid substances in solution, which render it in a chemical

sense impure. Such water is therefore unfit to be employed for the processes of solution and of washing precipitates, since any impurity thus introduced during the analysis would be detected and considered to have been present in the original substance.

The quantity of these impurities which is present in any particular water-supply will depend upon the nature of the soil with which the water has been in contact before its collection. The water-supply in some districts will be found to be almost perfectly pure, when it is subjected to the tests for impurity (31).

Rain-water which has fallen through pure air, and has been carefully collected, will yield little or no indication of dissolved impurity. The water-supply to the majority of laboratories will, however, be found to be unfit for analytical purposes, until it has been freed from dissolved solid substances by being subjected to the process of distillation.

In most towns distilled water can be purchased; but it is preferable to distil all the water required for use, either in the laboratory itself or in its immediate neighbourhood. For this purpose steam is generated and condensed by a suitable cooling arrangement.

The steam may be obtained from a steam-boiler which is in use for other purposes, or from a special copper boiler heated by solid or oil fuel or by a gas-burner. It is advantageous and economical to utilise the steam for heating the steam-ovens before it passes to the condenser: and water-stills are now made in all sizes, which effect these purposes satisfactorily.

The apparatus described in par. 1377 is now in general use in students' laboratories and is recommended both for convenience and for economical working.

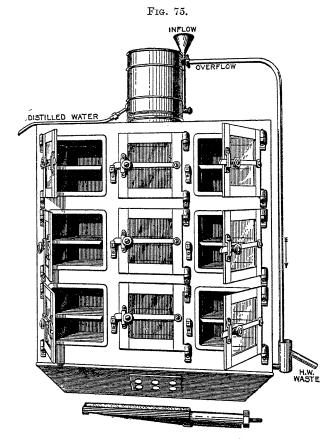
Smaller and simpler stills of a similar kind are obtainable when they are required for individual use only.

The hot outflow of condensing water from the still may be made to pass through a collecting-tank on its way to the waste service, and hot tap-water may then be drawn from this tank when required.

1377. **The Distillation of Water may be combined with the Heating of Steam-ovens and Steam-bath** by the following apparatus, known as the Brown-still, which may be conveniently placed in one of the open draught-recesses in the laboratory-wall.

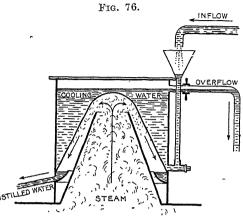
A front view of this still is shown in Fig. 75; and it will be seen that a shallow boiler, forming the bottom of a range of nine steam-ovens, is heated by a long Fletcher gas-burner. The steam passes from the boiler around the ovens, and is condensed by a special and very efficient condenser which is mounted on the top

of the range of steam-ovens, the distilled water thus produced being taken away by a pipe to a stoneware storage vessel. The top of the casing may have different-sized holes cut for dishes, and closed by lids when not in use: these serve for water-baths and hot plate (Figs. 26, 27, 28, par. 38), but they lessen the yield of distilled water.

FIG. 75.

THE BROWN STEAM-OVENS AND STILL.

There is an inflow of cold water from the water service to the bottom of the condenser, and the hottest water flowing away from the top of the condenser passes to a small feed-cylinder attached to the side of the boiler; a part of this water serves to maintain the level of water within the boiler, and the rest flows away through a hot-water storage tank into the waste service. The sectional drawing (Fig. 41, 48) will explain this feed-arrangement.

The sectional drawing (Fig. 76) renders evident the construction of the condenser, which exposes the steam to a large conical dome kept cold by the circulating water. The water formed by condensation in the dome is collected by an annular internal channel, which is connected with the outflow for the distilled water.

Fig. 76.

The Brown-condenser (in Section).

A detachable plate is screwed down over an opening in the boiler, and renders possible the removal of incrustation by scraping or by means of strong commercial hydrochloric acid diluted with four times its volume of water.

The oven-doors should be made of sheet-glass framed in copper, so as to render the interior of the ovens visible when the doors are closed; and in order to obtain a temperature near 100° C. in the oven, the air-inlet pipe to the ovens should be surrounded by steam so as to deliver heated air into the bottom of the ovens. An air-outlet is provided at the top of each oven.

The whole apparatus is made in sheet copper, and the interior surfaces of the condenser-dome and of the outflow pipe for the distilled water are thickly tinned to prevent contamination of the distilled water with copper.

When the gas-burner and supply of condensing-water have been properly adjusted, the apparatus may be allowed to work continuously without requiring any further attention.

RECOVERY OF SILVER AND PLATINUM FROM THEIR RESIDUES.

1378. Waste scraps of platinum and silver, and solutions and precipitates which contain these metals, should not be thrown away, but should be preserved in two large jars which are specially

reserved for them, and are labelled *Silver Residues* and *Platinum Residues* respectively. Platinum chloride and silver nitrate may be obtained from these residues by the methods described below.

SILVER RESIDUES.

1379. Some HCl is poured into the jar which contains the silver residues, and the acid is thoroughly mixed with the contents of the jar. The precipitate is then allowed to subside, and, after the liquid has been decanted, this precipitate is thoroughly washed by decantation : it may then be treated either by paragraph 1380 or 1381.

1380. The wet precipitate is rinsed into a flat shallow dish, and the layer of water is acidified with H_2SO_4. Strips of Zn, free from Pb, are then laid upon the silver precipitate, and the whole is allowed to stand quietly for several hours. The black spongy mass which remains is metallic silver : it is separated from any remaining Zn, and is washed until it is free from H_2SO_4.

This metallic deposit is dissolved by heating it with pure strong HNO_3, which has been diluted with its own measure of water. The solution is evaporated to dryness ; the solid residue is dissolved in water, and is once more evaporated to dryness in order to remove free acid completely. The residue is then dissolved in the proper proportion of water to give reagent 54 (1410). Any residue insoluble in HNO_3 is returned to the silver residue bottle.

1381. The well-washed precipitate which has been obtained from the silver residue bottle, after the addition of HCl in excess (1379), is filtered off and dried. It is then mixed with twice its weight of a mixture in equal proportions of K_2CO_3 and Na_2CO_3. This mixture is transferred to a clay crucible which is heated in a furnace. After the contents have been kept in a fused condition for four or five minutes, the crucible is removed and its bottom is tapped several times on a brick so as to cause the melted globules of Ag to unite. When the crucible is cool it is broken up, and the button of Ag is removed and well washed. It is then converted into $AgNO_3$-solution, as is described in paragraph 1380.

PLATINUM RESIDUES.

1382. The liquid in the platinum residue bottle is shaken up with the precipitate, and the whole is evaporated to dryness in a porcelain dish. The residue is then heated strongly for some time. When the dish is cool, water is poured upon the residue and boiled with it, and the aqueous solution is then decanted off. Solution of

oxalic acid is now poured upon the residue in the dish and evaporated to dryness, and the residue is once more strongly ignited.

The residue of metallic platinum is thoroughly washed with boiling water, and is dissolved by heating it with HCl, to which one-third its measure of HNO_3 has been added. The solution is evaporated to dryness over a water-bath. HCl is then poured in, and the liquid is once more evaporated to dryness and heated for some time on the water-bath. This residue, when dissolved in water, forms reagent 43 (1410).

Waste scraps of platinum foil and wire should be carefully preserved. They are cleansed by boiling them with HNO_3 and washing them well with water. They are then dissolved in a mixture of HCl and HNO_3, and converted into platinum chloride solution as is described above.

CHEMICALS AND REAGENTS.

1383. **In the Following Paragraphs general Directions** are given for the preparation of the reagents and of the test-substances which are required in the preceding Analytical Course.

Tabulated lists of the names and formulæ of these substances follow the general directions. A reference number is attached to each substance, and certain necessary details concerning its preparation and the tests for its purity are also supplied.

The pure chemicals which are required in analysis can be purchased, and it will be found more economical as a rule to buy them than to prepare them.

The preparation of the solutions and the dilution of acids and other liquids should, however, always be performed in the laboratory, since this lessens the cost both of purchase and of carriage.

Substances suitable for analysis are suggested in paragraphs 1415–1419.

1384. **Solution and Dilution.**—Many reagents and test-substances must be dissolved or diluted before they are used. As these processes of solution and dilution must be constantly carried out in a laboratory, it is important that the methods employed should be as simple and rapid in execution as possible, in order that the expenditure of labour and of time may be minimised.

It is also of great importance that the solutions should be of appropriate strength. It is usually advisable that the same liquid should be of different strengths when it is used as a reagent and as a test-solution. In either case a strength can be selected which generally yields the most satisfactory results. If the solution is

stronger than this, chemicals are wasted ; if it is weaker than this, the reaction may not be satisfactorily obtained. Hence it is advisable to keep these liquids in readiness for the student, rather than to leave him to prepare them doubtfully or wastefully when they are required.

And in order to lessen the time involved in preparing these solutions, it is well to make each solution in some quantity and to keep it in stock.

1385. **Normal Solutions.**—It is customary to prepare all solutions with a strength which is some multiple or submultiple of the strength of a "normal" solution; thus the strength may be three times normal, normal, half normal, one-tenth normal, and so on.

By a "normal" solution is meant a solution which contains one gram-equivalent per litre ; thus one litre of a normal solution of HCl contains 36·46 grams of HCl, one litre of a normal solution of Na_2CO_3 contains $\frac{Na_2CO_3}{2} = 56$ grams per litre, since this weight is chemically equivalent to 36·46 grams of HCl.

The advantage of adopting this system is that the volume of one solution which should be used to react *quantitatively* with another solution is known. Thus 1 c.c. of any normal acid-solution will neutralise 1 c.c. of a normal alkali-solution. Similarly 1 c.c. of normal $BaCl_2$- solution will precipitate quantitatively the sulphate in 1 c.c. of normal H_2SO_4.

1386. **The Apparatus required for Preparing Solutions** includes—

- A common balance, with earthenware pans, and the beam below.
- A more delicate balance.
- A set of brass weights from 1 kilogram to 1 gram.
- A strong measuring-cylinder to deliver one litre, and with graduations for every 5 cubic centimetres (c.c.).
- Several large wide-mouthed gallon (5 litre) jars, some of stoneware or earthen-ware, others of common green glass.
- Several large funnels of glass or of porcelain.

A convenient store-bottle for liquids is a well-cleansed *Winchester-quart*, the bottle in which acids and other liquids are constantly supplied to the laboratory.

The description of the processes for preparing liquid reagents is divided into (1) *Dilution of Liquids* (1387), (2) the *Solution of Solids* (1388–1393), and (3) the *Solution of Gases* (1394–1400).

DILUTION OF LIQUIDS.

1387. **In the Lists of Diluted Liquids which Follow,** the proportions by measure, in which the liquids are to be mixed with distilled water, are stated. Liquids may be mixed in these proportions by measuring them before they are mixed. But the process is often simplified by measuring the height from the bottom of the cylindrical vessel in which the mixture is to be made, to the level which the mixture is to reach. This height is then divided in the requisite proportion; and the division is marked by a file or a diamond, by a painted line, or by an india-rubber ring. Each liquid is then poured in to its own level, and the liquids are thoroughly mixed by shaking the bottle. The mark, when once made, will always serve for diluting the same liquid in the same vessel.

This method serves for numbers 2, 3, 4, 6, and 7 (1409).

In the preparation of dilute H_2SO_4 (1, 1409) special precautions are necessary, because the dilution of the strong acid produces much heat, see Remark 1 (1409).

SOLUTION OF SOLIDS.

1388. **In the Lists of Dissolved Solids which Follow,** the weight of the solid to be dissolved in water, and then made up to one litre in preparing each solution, is placed in the Fifth Column.

The number of grams of the solid to be dissolved in a Winchester-quart of water may be obtained by multiplying this weight by 2·4; since an average Winchester-quart bottle, filled about an inch above its shoulder, holds 2,400 c.c., or approximately 2,400 grams, of distilled water.

In a similar manner the weight of water held by any other bottle or vessel may be obtained with sufficient accuracy for this purpose by measuring its capacity in c.c., and counting this number as the weight of water in grams.

Pure solid chemicals are usually sold in the crystalline condition. Hence it may be assumed that the crystalline substance is to be used whenever this is possible.

1389. **If a Small Quantity of a Finely-powdered Solid** has to be dissolved, or if the solid is extremely soluble in water, the solution is often most simply made by introducing the weighed solid at once into the water contained in a stoppered bottle or a beaker, and then shaking or stirring the water until solution is completed. This method is successful with No. 12 (1409), with Nos. 19, 23, 27, 30, 43, 44, 49, 51, 54, 58, (1410), and with many of the substances in paragraphs 1411, 1412.

1390. **For Dissolving Large Quantities of Solids** two methods are described below. The first (1391) is useful when the solution must be rapidly prepared, and is of general application to the solution of solids; but the second (1392) is decidedly preferable for many reasons, and should always be employed if possible.

FIRST METHOD.

1391. Weigh out the required quantity of the solid substance, and heat it with distilled water in a large flat-bottomed flask on a sand- or water-bath with occasional shaking, or in a large porcelain dish over a Bunsen-burner with a rose top or over a Fletcher-burner.

This solution would often crystallise as it cooled, unless it is further diluted with water; hence, if it is not clear, it should either be filtered in a hot filter-jacket (see *Note*), or it may be at once poured into some cold distilled water contained in a large beaker, which has been marked to show the quantity of liquid required to fill the store-bottle.

While the liquid is being poured out of the dish, a wet glass rod should be held vertically and pressed against the lip of the dish, and the bottom of the dish should touch the top of the beaker. These precautions will prevent the liquid from running down outside the beaker.

Note.—**The Filter-jacket**, shown in Fig. 77, is a double-walled vessel, which is shaped to fit the funnel, and has a hollow projection (*a*) communicating with the interior of the jacket. Before the apparatus is used, it is about half filled with water, and supported on a tripod-stand. The water is then heated to boiling by placing a Bunsen-flame beneath the projection (*a*), which is filled with water communicating with that in the jacket. In this way hot water will circulate throughout the copper jacket, and the funnel supported within may be kept hot during filtration.

The solution is now diluted with distilled water to the required volume, if this has not been done already: the liquids are mixed well by stirring; and if the solution is turbid, it is covered and allowed to stand until it is clear. It is then poured or siphoned off into the store-bottle, the sediment being left behind.

FIG. 77.

THE FILTER-JACKET.

If the liquid is wanted in haste, it may be filtered into the bottle. For this purpose a double filter or a fluted filter may be used. If the liquid is filtered before it has been diluted to the full extent, the quantity to be passed through the filter will be lessened and time will be economised.

The Operation of Filtration, as it is described for ordinary

analytical purposes in paragraph 43, is very slow when a large quantity of a solid has to be separated from a liquid. This is partly due to the fineness of the pores of the filter-paper, and partly to the fact that the paper is in close contact with the sides of the funnel.

Methods are described below which serve better for dealing with large quantities of material to be filtered, such as are used in the preparation of pure chemicals and of stock solutions. It will be noticed that the procedure to be employed varies with the character of the solid.

Gelatinous or Non-granular Solids are conveniently separated from the liquids which contain them, by filtration through a large surface of fine linen.

One method for effecting this is shown in Fig. 78. The linen is first washed in hot water until it is free from glaze: it is then placed in a large funnel and made to assume the shape of a bag, as is shown by the dotted line. The bag is kept in its place by pressing a ring of wood firmly into the top of the funnel, as is shown in shaded section. When the filtration is finished, the bag may be squeezed so as to remove the adherent liquid more completely from the solid.

A simple modification of this method consists in making a square wooden frame about six inches across, and driving in a wire nail at each of its corners. The heads of the nails are then cut off so as to form four pins upon which the linen can be hung in the form of a bag. The funnel is thus dispensed with.

FIG. 78.

LINEN FILTER.

Granular or Crystalline Solids may be conveniently separated from the liquids which contain them, by means of a circular perforated porcelain plate 2 or 3 inches (4 to 7 c.m.) in diameter.

The perforated plate is dropped into the funnel and remains about 1¾ inches (4 cm.) from the apex of its conical interior surface.

The plate is then covered with a disc of filter-paper or of linen, which should be very slightly larger than the plate. After the moistened filter has been pressed into close contact with the inside of the funnel, the liquid which is to be filtered is poured upon the filter.

Filtration will take place much more rapidly in this filter, than in an ordinary paper filter which is in contact with the funnel by its whole aurface.

Perforated porcelain funnels, known as Buchner funnels, satisfactorily replace the combined perforated plate and funnel.

THE SECOND METHOD.

1392. This depends upon the fact that the density of the solution becomes greater as the quantity of solid dissolved in it is increased. Hence if the solid is immersed just beneath the surface of the water, a circulation of the liquid is produced. The water which has been in contact with the solid, and has been increased in density by dissolving it, constantly sinks and is replaced by the comparatively

lighter liquid from below. This circulation of water over the solid substance gradually dissolves it without the use of heat, and the process requires no attention after it has once been started. The process may be carried out as is described in (**a**), (**b**), or (**c**) below.

(**a**) The most simple method of applying this principle is to lay the weighed solid upon a piece of dry well-washed muslin. This is then tied up into a little bag, and is suspended in the upper part of the water contained in a jar of common stoneware or earthenware or of thick green glass. A glass rod placed across the mouth of the jar serves to hang the bag upon. The process of solution by this method is very rapid.

(**b**) A glass cylinder A (Fig. 79) which is open at both ends (such as a broken beaker, flask, or bell-jar) has one end covered with muslin, which is fastened on by a rubber ring and is shown by the lower dotted line. This cylinder with a muslin bottom is supported in the jar by means of two pieces of glass rod or tube, bent as is shown at *c c c*.

FIG. 79.

SOLUTION OF SOLID.

Distilled water is poured into the jar until it buries the muslin to the depth of about half an inch. The weighed substance is then placed in the cylinder, and the whole is allowed to stand until the solid has been dissolved. With large quantities of substance this will usually require several hours; with smaller quantities about twenty minutes or half an hour will be necessary.

(**c**) A convenient substitute for the glass cylinder with muslin bottom is an earthenware colander (Fig. 80). If the jar is too large, a stoppered bottle of suitable size may be placed in it so as to raise the water level sufficiently to reach the substance.

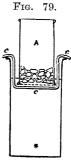
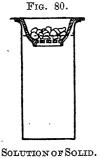



FIG. 80.

SOLUTION OF SOLID.

The processes of solution and filtration may be performed simultaneously by laying a piece of filter-paper on the bottom of the colander, or upon the muslin before it is fastened on the cylinder. The presence of even the coarsest filter-paper will, however, considerably retard the process of solution.

Large quantities of substance are most conveniently dissolved by starting the process overnight; the solution will then be completed by the morning. In this case the retardation caused by the filter-paper will be immaterial. The paper is, however, usually unnecessary, since any fine particles which have passed into the water will settle during the night, and

the liquid can therefore be easily decanted from the sediment.

It must be borne in mind that the volume of the water is increased by the solution in it of a salt, and especially by salts which contain water of crystallisation. Hence the quantity of water which is placed in the jar must be less than the volume of solution required, and the liquid must be made up to the required volume after the solution has been effected.

1393. **Preparation of Saturated Solutions of Solids.**—A solution is said to be saturated, when it contains the largest amount of the substance which the liquid can dissolve at the temperature of the solution. The quantity which can be dissolved usually varies widely with the temperature, and in the case of solid substances commonly increases with rise of temperature. Saturation is always understood to be effected at ordinary atmospheric temperature in the following text.

The methods described in paragraph 1392 are very convenient for the preparation of saturated solutions. The solution is known to be saturated when the solid supplied to the upper part of the liquid ceases to be any further dissolved.

In the case of a finely-powdered substance, which will remain long suspended in water, a saturated solution may be easily obtained by shaking the powder up with water. The powder is then allowed to subside, and the clear solution is decanted. The two following solutions may be prepared in this way.

1. *Calcium sulphate Solution*, No. 11 (1409), is made by filling a Winchester-quart up to its shoulder with distilled water, then pouring in some plaster-of-Paris powder, stoppering the bottle, and shaking it well. The liquid will remain milky for a long time; and since the water is thus kept in contact with a large surface of the solid it will become saturated with $CaSO_4$ before the powder has settled.

As soon as the liquid has become perfectly clear by settling, the solution is decanted into another bottle for use. The sediment remaining in the first bottle is again shaken up with a fresh quantity of water and the bottle is set aside. It will then furnish a fresh supply of the clear solution when necessary.

2. *Lime-water*, No. 36 (1410), is prepared by introducing freshly-slaked lime into a Winchester-quart bottle, filled to its shoulder with *tap-water*, and proceeding precisely as is described for the preparation of calcium sulphate solution in the preceding paragraph.

SOLUTION OF GASES.

1394. Many gases, which are more or less soluble in water, are most conveniently applied as reagents in the dissolved condition. Those solutions which are most frequently used, such as solution of ammonia, of hydrogen chloride and of sulphur dioxide, can be readily and cheaply purchased.

Of the remaining gaseous solutions: hydrogen sulphide solution should be kept in readiness, but the gas may be passed through the test liquid instead (1374). Nitrogen tetroxide solution is replaceable by a freshly-acidified solution of potassium or sodium nitrite. And as a substitute for chlorine-water, either bromine-water, or freshly-acidified solution of bleaching-powder may be employed.

It will be seen, therefore, that the preparation of gaseous solutions is by no means indispensable.

1395. **Preparation of Saturated Solutions of Gases.**—All the solutions of gases (1396–1400) should be prepared in the open air or under a good draught, since the gases have an unpleasant smell and are injurious when inhaled.

Each gas is made to pass from the generating apparatus down a delivery tube (*a*, *b*, Fig. 81) *to the bottom* of some cold distilled water, contained in a bottle which can be closed by a well-fitting stopper. The water is kept cool, if necessary, by immersing the bottle in a pan of cold water. Bubbles of gas are thus made to pass in a rapid stream through the whole height of the liquid, and a portion at least of each bubble is dissolved.

FIG. 81.

c a b

SATURATION OF WATER WITH GAS.

The solution is saturated as soon as the gas is not further dissolved. This may be judged in some cases by observing whether the bubbles cease to diminish in size during their ascent through the liquid. But a better test of saturation consists in withdrawing the delivery-tube, at once closing the bottle with the stopper or the thumb, and shaking it well. If pressure is felt from within, due to the liberation of some of the dissolved gas by the agitation, the solution is saturated. But if suction from within is felt, due to the solution of the gas filling the upper part of the bottle, the liquid is not yet saturated with the gas.

1396. **Saturated Solution of Hydrogen sulphide** (No. 31, 1410) is made by passing the gas from the apparatus described in par. 1371 or 1372 through water (Fig. 81) until the liquid is saturated (1395). The solution should be prepared in small quan-

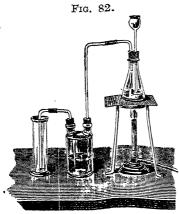
tity only, since the gas gradually undergoes decomposition, attended with deposition of sulphur, by the oxygen dissolved from the air.

1397. **Sulphurous acid Solution** (No. 8, 1410) is prepared by passing SO_2 into cold water (1395). The gas may be made by heating copper turnings or clippings with strong H_2SO_4 in the flask shown in the apparatus in Fig. 82, and passing the gas through water in the washing-bottle.

This solution is kept in stock for pharmaceutical purposes, and may therefore be readily purchased. Cylinders of liquid SO_2 may also be purchased, and the gas which it evolves by spontaneous evaporation, when the valve is opened, may be employed for preparing the saturated solution.

1398. **Chlorine-water** (No. 22, 1410) is made by passing chlorine into cold water until the liquid is pale yellow in colour.

The apparatus for preparing the gas is shown in Fig. 82. Manganese dioxide in lumps is placed in the flask, and is covered with commercial hydrochloric acid diluted with an equal volume of water. The contents of the flask are then gently heated, and the gas is washed by passing it through a little water in the two-necked bottle.

FIG. 82.

PREPARATION OF SULPHUR DIOXIDE OR CHLORINE.

The gas may also be obtained from a cylinder of liquid chlorine.

Chlorine - water is rapidly changed in daylight into solution of hydrochloric acid, with escape of oxygen. The liquid must therefore be kept in a perfectly dark place, or in a bottle which is shielded from light by an opaque covering.

For many purposes bromine-water (No. 17, 1410) may be substituted for chlorine-water, and is much more easily prepared and preserved. Another substitute for chlorine-water is a little bleaching-powder shaken up with water in a test-tube and acidified with dilute HCl or HĀ.

1399. **Nitrogen tetroxide Solution** (No. 42, 1410).—Lead nitrate in dry powder is heated in a test-tube fitted with a cork and delivery-tube (Fig. 83). The reddish-brown gas which escapes is passed into dilute H_2SO_4.

Care must be taken to maintain the heat uniformly after the

fumes begin to be evolved, else the liquid may be sucked back into the hot tube by the contraction of the gas on cooling. For

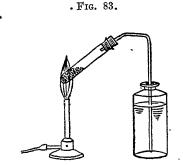
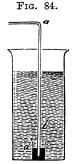
FIG. 83.

SOLUTION OF NITROGEN TETROXIDE.

FIG. 84.

PASSING SILICON FLUORIDE INTO WATER.

the same reason the delivery-tube must be removed from the liquid as soon as the heating is stopped.

This solution need not be saturated with the gas.

1400. **Hydrofluosilicic acid** (No. 6, 1410) is made by passing silicon fluoride gas into water. The gas is prepared in a flask fitted as is shown in Fig. 83. An intimate mixture of 50 grams of dry, pure, finely-powdered fluorspar with 50 grams of fine white sand is poured into this flask; 300 grams of strong H_2SO_4 are then introduced through the funnel tube, and the acid is thoroughly mixed with the powder by shaking it round in the flask.

SiF_4 is evolved when the flask is heated by a small flame from a rose-burner, or more safely on a sand-bath. The gas passes first through the two-necked bottle (Fig. 82), which must be empty and dry inside, thence through a bent tube *ab* (Fig. 84), which is fitted upon the outlet tube of the bottle by a rubber joint. The end of the tube (*ab*) dips into mercury contained in a small beaker *d* (Fig. 84), which stands in a large beaker containing 400 c.c. of water.

As soon as the silicon fluoride escapes from the mercury, and comes into contact with the water, it forms hydrofluosilicic acid which dissolves in the water, and silicic acid which remains suspended in the water as a gelatinous mass. The silicic acid would soon stop the escape of the gas, if the end of the delivery-tube were not protected from contact with water by being immersed in mercury.

When the current of gas slackens, the heat is raised until white fumes of H_2SO_4 begin to appear in the preparation flask. The process is then arrested, and the gelatinous matter is separated

from the liquid in the beaker. This is effected by squeezing the liquid through fine muslin, and then filtering, if necessary, to make it quite clear.

The silicic acid may be dried, heated strongly in a porcelain dish, and put by in a stoppered bottle for use as a reagent (No. 53, 1410).

STORE-JARS AND BOTTLES.

1401. **Stock of Solid Chemicals.**—The broad-necked common green-glass jars with flat stoppers, which are used for preserves and confectionery, may be used as store-jars for large quantities of solid chemicals. The jars are cheap and strong, and present the advantage over stoneware-jars that the quantity of material which they contain is seen at a glance. The flanged stoppers exclude dust and can be made air-tight by fastening a cork ring around their lower part. The complete exclusion of air is, however, seldom necessary.

These jars can be purchased in several convenient sizes. Solids are readily removed from them by means of wooden spoons or horn scoops.

1402. **Solids for Analysis.**—The 1 lb. glass honey-jars with glass caps serve well for keeping smaller quantities of solids, and can be made air-tight by means of a cork strip fastened round the neck. These jars serve for storing the solid powders which are required for analysis in the laboratory (1415–1419): their necks should be of sufficient size to allow of the insertion of an ordinary watch-glass to remove some of the contents.

1403. **Reagents and Test-solutions.**—Well-made white-glass bottles should be used for the Reagents and Test-solutions. The bottles should have flat-headed stoppers which protect the lip from dust, and each stopper should be well ground into the bottle so as to ensure its fitting. Stopper and bottle are prevented from permanently parting company by having an identical number etched upon them.

Accurately fitting glass stoppers should not be used in bottles containing solution of KOH- or NaOH-solution, since they are certain to be set fast. The use of a loosely fitting glass stopper, made to fit by surrounding it with a piece of rubber tube, obviates this difficulty.

The liquid bench reagents (1409) may be kept in narrow-necked bottles of 6 or 8 ounces (200 or 250 c.c.) capacity, and the solids in 4-ounce (120 c.c.) broad-necked bottles. The general reagents (1410) should be in 10 or 12-ounce (300 or 400 c.c.) bottles. The test solutions (1411, 1412) require larger bottles of about 32-ounce (1000 c.c.) capacity.

1404. **Stock Bench-reagent Solutions.**—The bench-reagent solutions (1409) may be conveniently kept in stock in an accessible position in the laboratory in large glass jars with glass taps below.

These taps may be ground into a tubulure near the bottom of the bottle, and after the perfectly dry tap has been greased and inserted, it is fastened in the tubulure by applying externally a thick coating of paraffin wax. The plug and seat of the stopper require to be occasionally perfectly dried and then greased. Or the taps may be inserted through a rubber cork which has been bored and placed in the tubulure. The storage of the bench-reagents in large stock-jars enables each student to fill his own bench-bottles when necessary.

1405. **Stock-bottles for General Reagent- and Test-solutions.**—These solutions may be made of double strength and may be kept in Winchester-quart bottles. When required for use a solution is diluted with an equal volume of water.

LABELLING BOTTLES.

1406. **Every Bottle in use in the Laboratory should be Labelled.**—Beginners are much assisted if the label bears not only the name but also the chemical formula of the substance which is contained in the bottle. It is also convenient to legibly number each bottle in the series. This number serves as a short means of reference. If the edges of the shelves are numbered to correspond with the bottles which should stand on them, the bottles are easily kept in their places and are quickly found when they are required.

The label should also give the strength of the solution in terms of normality (1385).

The gummed labels should be stored in a dry place. When

the label is used, the whole of the gummed surface should be wetted and made to adhere to the bottle by pressure with a clean cloth. The label is then allowed to dry thoroughly, and is protected by being brushed rapidly across with an ordinary broad flat and stiff gum-brush, which has just been taken out of a dish of melted paraffin wax. A thin coating of the wax is thus made to entirely cover the label and to project for a short distance beyond its edge upon the glass surface.

A little practice will render it possible to lay on an even layer of the wax, which does not penetrate and stain the paper. If the paraffin is heated only slightly above its melting-point, it will set too rapidly to penetrate the paper.

This paraffin varnish, if properly applied, perfectly resists the action of water, acids and alkalis. In fact, it can only be removed or injured by mechanical means, by heat, or by such solvents as ether and turpentine.

Bottles containing the strong mineral acids commonly have the name or formula etched upon their surface. This is costly and it is unnecessary, since the paraffined paper label resists the action even of strong acids.

Names and formulæ painted on bottles with Japan-black are also permanent in the laboratory.

LISTS OF REAGENTS AND CHEMICALS.

1407. The following paragraphs (1408–1414) give particulars of the reagents and chemicals required for the foregoing course of analytical work.

The chemicals required for Section II (1408), with a few exceptions, will be found by the reference figures in the later lists.

The chemical solutions and solids required for Section III fall into the following three classes:—

1. The Bench Reagents (1409) are those most frequently required for use by the student, and a set is therefore supplied to each working-bench. These bottles should be refilled when necessary by the student from the store-bottles (1404).

2. The General Reagents (1410) are not required so frequently; and one set, conveniently placed, will suffice for about fifteen students.

3. The Test-solutions and Solids (1411, 1412) are supplied for trying the reactions for metals and acid-radicles by means of the above reagents. There should be a set of these for every fifteen students in a convenient position in the laboratory. An (s) placed against the number means that the substance is required in the solid state as well as in solution: the solids may be in powder contained in 4-ounce (120 c.c.) wide-mouthed bottles.

It will be seen that the Bench Reagents, the General Reagents, and the Test Chemicals are placed in alphabetical order after the acids, each having an initial letter and a distinctive number.

The label of each bottle should carry this distinctive letter and number, and these should also be placed on the front edge of the shelf at the spot where the bottle should stand, as this keeps each bottle in its place and facilitates finding it. It is well also to state on the label of solutions the strength of the solution in the bottle.

The tabulated lists are arranged as follows :—

Column 1 gives the reference number and letter of the bottle.

Column 2 gives the name of the substance.

Column 3 gives the formula of the substance.

Column 4 gives the relation of the strength of the solution to normality (1385).

Column 5 gives the weight or volume of the substance to be contained in one litre of water.

Column 6 gives special information, when it is necessary.

The directions for making the solutions will be found in paragraphs 1384 *et seq.*

CHEMICALS REQUIRED FOR SECTION II.

1408. The following substances are required for the experiments in Section II.: they are placed in the order in which they are required for use by the student who is working through that section. When a reference number is affixed, it indicates that the substance will be found in one of the following lists. A letter (s) signifies that a soluble substance is required in the solid state.

It will be seen that only filter-paper, mercuric oxide, barium sulphate, wood charcoal and zinc oxide need be specially supplied, as the remaining substances are provided for in the subsequent lists.

Name.	Reference Number.
Potassium nitrate (s)	17, 1412
Copper sulphate (s)	12, 1411
Marble	39, 1412
Hydrochloric acid	2, 1409
Copper	24, 1410
Nitric acid	3, 1409
Barium chloride	10, 1409
Ammonium carbonate	8, 1409
Filter-paper	—
Sulphuric acid	1, 1409
Mercuric oxide	—
Ammonium chloride (s)	2, 1411
Potassium chloride (s)	21, 1411
Sodium carbonate (s)	21, 1409
Barium sulphate	—
Manganese dioxide	38, 1410
Borax (s)	18, 1409
Ferrous sulphate (s)	14, 1411
Sodium chloride	24, 1411
Wood charcoal	—
Lead acetate (s)	15, 1411
Ammonium hydroxide	6, 1409
Litmus-paper } Turmeric-paper }	22, 1409
Zinc oxide	—

1409. REAGENTS REQUIRED

The liquid reagents may be in 6 oz. (200 c.c.

1. Reference number.	2. Name. [The small numbers in brackets refer to remarks in column 6.]	3. Chemical Formula.
Liquids.		
1	Acid, Sulphuric (1)	H_2SO_4
2	Acid, Hydrochloric (2)	HCl
3	Acid, Nitric (3)	HNO_3
4	Acid, Acetic (4)	$HC_2H_3O_2$ or $H\bar{A}$
5	Ammonium chloride (5)	NH_4Cl
6	Ammonia, or Ammonium hydroxide (6)	NH_4OH
7	Ammonium sulphide (7)	$(NH_4)_2S$
8	Ammonium carbonate (8)	$(NH_4)_2CO_3$
9	Ammonium oxalate	$(NH_4)_2C_2O_4.H_2O$
10	Barium chloride	$BaCl_2.2H_2O$
11	Calcium sulphate	$CaSO_4$
12	Potash, or Potassium hydroxide (9)	KOH
13	Potassium chromate	K_2CrO_4
14	Potassium ferrocyanide	$K_4FeCy_6.3H_2O$
15	Potassium ferricyanide (10)	K_3FeCy_6
16	Sodium phosphate (11), or	$Na_2HPO_4.12H_2O$
	Sodium ammonium phosphate	$NaNH_4HPO_4.4H_2O$
17	Sodium carbonate	$Na_2CO_3.10H_2O$ (crystals)
Solids.		
18	Borax (12)	$Na_2B_4O_7$
19	Potassium chlorate	$KClO_3$
20	Reduction mixture (60)	Na_2CO_3+KCN
21	Sodium carbonate (13)	Na_2CO_3
22	Test-papers (51)	—

FOR EACH BENCH.

bottles: the solids in 4 oz. (120 c.c.) bottles.

Reference Number.	4. Strength in normality (N) (1385).	5. Condition; and weight of solid in grams, or volume of liquid in cc. dissolved to one litre.	6. Remarks. [The small numbers refer to corresponding numbers in column 2.]
Liquids.			
1	3 N	83 c.c.	1. Pure strong H_2SO_4 (Sp. gr. 1·84) is used; it must be gradually poured in the proper proportion into water contained in a large thin beaker or an earthen jar, while constantly stirring the water. The hot liquid is cooled by immersing the vessel in cold water, and is then poured into the store bottle. If the acid is pure, no white precipitate of $PbSO_4$ will form during dilution.
2	3 N	303 c.c.	2. Pure strong HCl (Sp. gr. 1·16) is used; it must be colourless, and give, after dilution, no precipitate with either $BaCl_2$ or H_2S, and no colour with KCNS-solution.
3	3 N	188 c.c.	3. Pure strong HNO_3 (Sp. gr. 1·42) is used; it must give no precipitate, after dilution, with $BaCl_2$- or $AgNO_3$-solution, added to separate portions, and no colour with KCNS-solution.
4	3 N	840 c.c.	4. Pure acetic acid (Sp. gr. 1·04) is used; it must give no precipitate or coloration with Am_2S.
5	3 N	160·5 grams.	5. Must give no precipitate with $BaCl_2$-solution.
6	3 N	143 c.c.	6. Must give only a very slight precipitate with lime-water, no coloration with Am_2S, and separate portions acidified with HNO_3 must give no precipitates with $BaCl_2$- and with $AgNO_3$-solution. "Liquor ammoniæ fortissima," of 880° specific gravity, is used for dilution with water.
7	—	500 c.c.	7. Must be yellow, and give with acids H_2S and a white precipitate of S; it must give no precipitate with solutions of Ca- or Mg-salts.
8	3 N	120 grams.	8. Solid Am_2CO_3 is dissolved by the second method (1392) in cold water, but in diluting, one-fourth of the bottle must be filled with strong AmOH.
9	N	77 grams.	9. White "stick potash" is used.
10	N	122 grams.	10. Dissolve a small piece of solid just before use; it must give no blue precipitate with $FeCl_3$-solution.
11	N/20	Saturated (1393).	11. Its solution must yield no precipitate with AmOH.
12	3 N	120 grams.	12. The borax is best dried by heating it in a platinum or porcelain dish, until, after melting, it has again become solid; this solid mass is then finely powdered in a mortar and kept in a stoppered bottle.
13	N	97 grams.	13. Dry finely-powdered sodium carbonate. It must, after having been dissolved in excess of HNO_3, give no precipitate with $BaCl_2$,- or $AgNO_3$,-or $AmHMoO_3$-solution (571); and if evaporated with excess of HCl must leave no residue insoluble in dilute HCl (646).
14	N	606 grams.	
15	—	In small pieces.	
16 {	N	119 grams.	
	N	70 grams.	
17	3 N	429 grams.	
Solids.			
18	—	In powder.	
19	—	In small crystals.	
20	—	In powder.	
21	—	In powder.	
22	—	Blue and red litmus, and turmeric, in small strips.	

1410. GENERAL REAGENTS FO[R]

These reagents may be contained in 10

1. Reference Number.	2. Name. [The small numbers in brackets refer to remarks in column 6.]	3. Chemical Formula.
A 1	Acid, Hydrochloric (1)	HCl (Sp. gr. 1·16)
A 2	Acid, Nitric (2)	HNO_3 (Sp. gr. 1·42)
A 3	Acid, Sulphuric (3)	H_2SO_4 (Sp. gr. 1·84)
A 4	Acid, Acetic (4)	$HC_2H_3O_2$, or $H\bar{A}$
A 5	Acid, Hydrofluoric (5)	HF
A 6	Acid, Hydrofluosilicic (6)	H_2SiF_6
A 7	Acid, Oxalic	$H_2C_2O_4.2H_2O$
A 8	Acid, Sulphurous	H_2SO_3
A 9	Acid Tartaric (7)	$H_2C_4H_4O_6$, or $H_2\bar{\bar{T}}$
A 10	Acid, Sodium tartrate (8)	$NaHC_4H_4O_6.H_2O$
A 11	Alcohol, Rectified spirit (9)	C_2H_6O
A 12	Ammonium acetate	$NH_4C_2H_3O_2$
A 13	Ammonium chloride (1313)	NH_4Cl
A 14	Ammonium molybdate (10)	$(NH_4)_2MoO_4$
B 15	Barium carbonate (11)	$BaCO_3$
B 16	Barium peroxide	BaO_2
B 17	Bromine-water (12)	Br-water
C 18	Calcium carbonate (1314)	$CaCO_3$
C 19	Calcium chloride	$CaCl_2.6H_2O$ (crystals)
C 20	Calcium fluoride	CaF_2
C 21	Carbon disulphide	CS_2
C 22	Chlorine-water	Cl-water
C 23	Cobalt nitrate (13)	$Co(NO_3)_2.6H_2O$
C 24	Copper	Cu
C 25	Copper sulphate	$CuSO_4.5H_2O$
E 26	Ether, methylated	$(C_2H_5)_2O$
F 27	Ferric chloride (14)	$FeCl_3.6H_2O$
F 28	Ferrous sulphate (15)	$FeSO_4.7H_2O$
F 29	Fusion mixture (16)	$Na_2CO_3+K_2CO_3$
G 30	Gold chloride	$AuCl_3$
H 31	Hydrogen sulphide (17)	H_2S-water
I 32	Indigo-solution	—

METALS AND ACID-RADICLES.

r 12 oz. (300 or 400 c.c.) bottles.

Reference Number.	4. Strength in normality (N) (1385).	5. Condition; and weight in grams dissolved to one litre.
A 1	10 N	Strong, pure.
A 2	16 N	Strong, pure.
A 3	36 N	Strong, pure.
A 4	3 N	Strong, pure
A 5	—	—
A 6	—	See par. 1400.
A 7	N	63 grams.
A 8	N/3	Saturated solution (1397).
A 9	—	In small pieces.
A 10	—	Saturated solution.
A 11	—	Strong.
A 12	N	77 grams.
A 13	—	In powder.
A 14	—	—
B 15	—	—
B 16	—	In powder.
B 17	—	—
C 18	—	In powder.
C 19	N	110 grams.
C 20	—	In powder.
C 21	—	—
C 22	—	See par. 1398.
C 23	N	145 grams.
C 24	—	Small strips of sheet copper.
C 25	N	125 grams.
E 26	—	—
F 27	N	90 grams.
F 28	—	In small pieces.
F 29	—	—
G 30	—	In dilute solution.
H 31	—	See par. 1396.
I 32	—	Indigo-carmine dissolved in water.

6. Remarks.

[The numbers refer to corresponding small numbers in brackets in column 2.]

1. See remark 2 (1409).
2. See remark 3 (1409).
3. Must be colourless, and give no brown ring when it is poured below some $FeSO_4$-solution (509).
4. See remark 4 (1409).
5. Purchased and kept in gutta-percha bottles.
6. Must give no precipitate with $Sr(NO_3)_2$-solution.
7. The crystallised acid must be freshly dissolved.
8. $Na\overline{HT}$ must be shaken with water in the bottle, in sufficient quantity to leave a layer of solid below.
9. Strong rectified methylated spirit, which must leave no residue on evaporation and must remain clear when it is diluted with water.
10. 10 grams. of Am_2MoO_4 are dissolved in 125 c.c. of strong AmOH, which has been previously mixed with an equal volume of water; the solution is then allowed to stand if necessary until it is clear, and is then poured off into 500 c.c. of strong HNO_3; the liquid will become hot, and must be cool before it is used.
11. Pure $BaCO_3$-powder is purchased, or is made by precipitating $BaCl_2$-solution completely with Am_2CO_3-solution, and washing by decantation. This powder is then mixed with water to a creamy liquid.
12. A few drops of Br are dissolved by shaking them up with water in the bottle. Sodium hypochlorite (Na_2Cl_2O), commercial "Liquor sodae chlorinatae" may be generally used (311), but it does not keep well.
13. The bottle should be closed by a loosely-fitting rubber stopper, which is perforated to hold a glass tube passing through and dipping into the liquid. By closing the open end of the tube with the finger and removing the tube some liquid is taken out, and a drop may be delivered by carefully relaxing the pressure of the finger.
14. Remove free acid if necessary, by adding AmOH with constant stirring until the last drop produces a precipitate of $Fe(OH)_3$, and then filtering.
15. Clean small crystals; a small piece is crushed and dissolved in cold water immediately before use.
16. The dry finely-powdered carbonates are intimately mixed in the proportion of 53 : 69, and the mixture is kept in a stoppered bottle.
17. The liquid must not darken when it is mixed with AmOH.

1410. (*Continued.*) GENERAL REAGENTS FO

1. Reference Number.	2. Name. [The small numbers in brackets refer to remarks in column 6.]	3. Chemical Formula.
L 33	Lead acetate	$Pb(C_2H_3O_2)_2.3H_2O$
L 34	Lead acetate in potash [18]	$Pb\bar{A}_2+KOH$
L 35	Lead nitrate	$Pb(NO_3)_2$
L 36	Lime-water	$Ca(OH)_2$
M 37	Magnesium sulphate	$MgSO_4.7H_2O$
M 38	Manganese dioxide [19]	MnO_2
M 39	Marble	$CaCO_3$
M 40	Mercuric chloride	$HgCl_2$
M 41	Microcosmic salt [20]	$NaNH_4HPO_4.4H_2O$
N 42	Nitrogen tetroxide solution	N_2O_4-solution
P 43	Platinum chloride (*Note*, 420)	$PtCl_4$
P 44	Potassium chloride	KCl
P 45	Potassium cyanide [21]	KCN
P 46	Potassium dichromate	$K_2Cr_2O_7$
P 47	Potassium hydrogen sulphate	$KHSO_4$
P 48	Potassium ferricyanide	K_3FeCy_6 (1409, 15)
P 49	Potassium iodide	KI
P 50	Potassium nitrate	KNO_3
P 51	Potassium nitrite [22]	KNO_2
P 52	Potassium thiocyanate	$KCNS$
S 53	Silica, white sand (1400)	SiO_2
S 54	Silver nitrate	$AgNO_3$
S 55	Slaked lime [23]	$Ca(OH)_2$
S 56	Sodium acetate	$NaC_2H_3O_2.3H_2O$
S 57	Sodium acetate and acetic acid [24]	$Na\bar{A}$ and $H\bar{A}$
S 58	Sodium hydroxide, pure [25]	$NaOH$
S 59	Sodium nitrate, solid	$NaNO_3$
S 60	Stannous chloride [26]	$SnCl_2.2H_2O$
S 61	Starch [27]	—
S 62	Steel [28]	Fe
W 63	Wax, paraffin- or bees-wax.	—
Z 64	Zinc [29]	Zn
Z 65	Zinc sulphate	$ZnSO_4.7H_2O$

METALS AND ACID-RADICLES.

Reference Number	4. Strength in normality (N) (1385).	5. Condition; and weight in grams dissolved to one litre.
L 33	N	190. Clear by adding $H\bar{A}$.
L 34	—	—
L 35	—	Small pieces.
L 36	N/20	Saturated solution (1393).
M 37	N	123 grams.
M 38	—	Solid, in powder
M 39	—	Pea-sized pieces.
M 40	N/5	27 grams.
M 41	—	In powder.
N 42	—	See par. 1399.
P 43	—	[Costly, use with care.]
P 44	N	75 grams.
P 45	—	In small pieces or powder.
P 46	N	49grms. Andsolid
P 47	—	Small pieces.
P 48	—	Small pieces.
P 49	N/10	17 grams.
P 50	—	In small pieces.
P 51	N	85 grams.
P 52	N	97 grams.
S 53	—	In fine powder.
S 54	N/10	17 grams.
S 55	—	In powder.
S 56	N	65 grams
S 57	—	—
S 58	3 N	120 grams.
S 59	—	In small crystals,
S 60	N	112·5 grams.
S 61	—	In powder.
S 62	—	—
W 63	—	In pieces.
Z 64	—	Strips, rods, or granulated.
Z 65	N	145 grams.

6. Remarks.
[The numbers refer to corresponding small numbers in brackets in column 2.]

18. Add to some of the above warm $Pb\bar{A}_2$-solution (L 33) KOH-solution (12, 1409) with constant stirring, until the precipitate just redissolves. Prepare in small quantity only when required (480, *Note*).
19. Fine powder; must not evolve CO_2 or Cl when it is warmed with strong H_2SO_4.
20. The solution in HNO_3 must give no precipitate with $AgNO_3$-solution.
21. Dissolve a small piece by warming it with water immediately before use.
22. Make in small quantity only, or immediately before use, as the solution changes. It must give abundant red fumes when mixed with dilute H_2SO_4.
23. Freshly burnt pieces of lime are placed upon a plate, and water is poured upon them until they begin to appear moist on the surface; the superfluous water is then drained off, and as soon as the lime has crumbled to powder and cooled, it is placed in a broad-mouthed stoppered bottle.
24. Dissolve 20 grams of sodium acetate crystals in 60 c.c. of distilled water, and add 40 c.c. of strong $H\bar{A}$ (A 4).
25. This solution should be kept in a green glass bottle as it dissolves Pb from colourless flint glass; and a rubber or loose stopper is preferable to an ordinary ground-in glass stopper, as this becomes fixed. The solution must not darken in colour with H_2S, or give gelatinous $Al(OH)_3$ when it is mixed with AmCl-solution (1409, 5).
26. $SnCl_2$-crystals are dissolved in water containing HCl, and the solution is kept with immersed tin fragments and excluded from air.
27. Make before use by stirring 2 grams of starch-powder, made into paste with water, into 100 c.c. of boiling water, and cool.
28. Short lengths of broken knitting-needles, kept with quick-lime to prevent rusting.
29. Must be free from arsenic (176, 177, 178).

1411. SOLUTIONS FOR THE

These solutions may be kept in 32 oz. (1000 c.c.) bottles, each of which is labelled
Each substance with (s) affixed in column 1 should also be provided as a solid in

1. Reference Number.	2. Name. [Small numbers in brackets refer to remarks in column 6.]	3. Chemical Formula.
A 1.s	Aluminium potassium sulphate	$AlK(SO_4)_2.12H_2O$
A 2.s	Ammonium chloride	AmCl
A 3.s	Antimonious chloride (1)	$SbCl_3$
A 4.s	Arsenious oxide in HCl (2)	As_4O_6
A 5	Arsenious oxide in H_2O (3)	As_4O_6
B 6	Barium chloride	$BaCl_2.2H_2O$
B 7.s	Bismuth nitrate (4)	$Bi(NO_3)_3.5H_2O$
C 8.s	Cadmium sulphate	$CdSO_4.4H_2O$
C 9	Calcium chloride	$CaCl_2.6H_2O$
C 10.s	Chromium potassium sulphate	$CrK(SO_4)_2.12H_2O$
C 11	Cobalt nitrate	$Co(NO_3)_2.6H_2O$
C 12.s	Copper sulphate	$CuSO_4.5H_2O$
F 13	Ferric chloride	$FeCl_3.6H_2O$
F 14.s	Ferrous sulphate (5)	$FeSO_4.7H_2O$
L 15.s	Lead acetate (6)	$Pb(C_2H_3O_2)_2.3H_2O$
M 16.s	Magnesium sulphate	$MgSO_4.7H_2O$
M 17.s	Manganese chloride	$MnCl_2$
M 18.s	Mercuric chloride	$HgCl_2$
M 19	Mercurous nitrate (7)	$Hg_2(NO_3)_2.H_2O$
N 20.s	Nickel sulphate	$NiSO_4.7H_2O$
P 21.s	Potassium chloride	KCl
S 22	Silver nitrate	$AgNO_3$
S 23.s	Sodium arsenate	$Na_2HAsO_4.12H_2O$
S 24.s	Sodium chloride	NaCl
S 25	Stannic chloride (8)	$SnCl_4$
S 26.s	Stannous chloride (9)	$SnCl_2.2H_2O$
S 27	Strontium nitrate	$Sr(NO_3)_2.4H_2O$
Z 28.s	Zinc sulphate	$ZnSO_4.7H_2O$

REACTIONS OF THE METALS.

with the number, name, formula and normality-strength of the solution (1385).
a 4 oz. (120 c.c.) wide-mouthed bottle similarly labelled.

Reference Number	4. Strength in normality (N). (**1385**).	5 Weight in grams dissolved in one litre of water.
A 1.s	N	118.
A 2.s	N	54.
A 3.s	N/5	15.
A 4.s	N/5	7.
A 5	—	Saturated.
B 6	N	122.
B 7.s	N/5	30.
C 8.s	N/5	26.
C 9	N/2	55.
C 10.s	N/5	20.
C 11	N/5	29.
C 12.s	N/5	25.
F 13	N/2	45.
F 14.s	N/5	In small pieces.
L 15.s	N/5	38.
M 16.s	N	13.
M 17.s	N/5	40.
M 18.s	N/5	29.
M 19	N/5	56.
N 20.s	N/5	28.
P 21.s	N	75.
S 22	N/5	34.
S 23.s	N/5	27.
S 24.s	N	58.
S 25	N/2	45.
S 26.s	N/5	23.
S 27	N	141.
Z 28.s	N/5	29.

6. Remarks.
[The numbers refer to corresponding small numbers in brackets in column 2.]

1. 5 grams of $SbCl_3$ crystals are dissolved in 25 c.c. of strong HCl diluted with 25 c.c. of water, and the solution is diluted to a litre with strong HCl diluted with four volumes of water. For tests on the solid, Sb_2O_3 or SbOCl is used.
2. Dissolve the As_4O_6 by heating it with 25 c.c. of strong HCl diluted with 25 c.c. of water, and dilute to a litre.
3. Boil the As_4O_6 for some minutes with 1000 c.c. of water and filter into the bottle.
4. The $Bi(NO_3)_3$ is dissolved by heating it with 25 c.c. of strong HCl diluted with 25 c.c. of water: this is cooled and poured into the bottle, and the volume is made up with water containing $\frac{1}{20}$th its volume of strong HCl. For the solid, $BiONO_3$ is used.
5. A small crystal of $FeSO_4$ (F 28, **1410**) is crushed and dissolved in cold water just before it is used.
6. Some HA must be added to clear the solution.
7. Dissolve 56 grams of $Hg_2(NO_3)_2$ by warming it with 6 c.c. of strong HNO_3 diluted with 114 c.c. of water, then dilute with water to a litre. Keep drops of Hg at the bottom of the bottle.
8. Heat 28 grams of $SnCl_2$ with 25 c.c. of strong HCl and 100 c.c. of water, adding powdered $KClO_3$ gradually with constant stirring, until the liquid turns yellow and Cl is smelt: then boil off the Cl, and dilute to one litre.
9. Boil 23 grams of $SnCl_2$ with 25 c.c. of strong HCl diluted with 25 c.c. of water, and dilute the clear solution to one litre. Keep scraps of tin in the bottle.

1412. SOLUTIONS FOR THE

These solutions may be kept in 32 oz. (1000 c.c.) bottles, each of which is labelled
Each substance with an (s) affixed in column 1 should also be provided as a solid
ist occur in the preceding tables, as is shown by the references in square brackets
reference; but it is more convenient to make up this set complete, as below, if
chemical name is placed before the metal in this list, the ordinary chemical name

1. Reference Number.	2. Name. [Small numbers in brackets refer to column 6. References in square brackets to preceding Tables.]		3. Chemical Formula.
A 1.s	Acetate, sodium	[56, 1410]	$NaC_2H_3O_2.3H_2O$
A 2	Arsenate, sodium	[23, 1411]	$Na_2HAsO_4.12H_2O$
B 3.s	Borate, sodium	[18, 1409]	$Na_2B_4O_7.10H_2O$
B 4.s	Bromide, sodium		$NaBr$
C 5	Carbonate, calcium (marble)	[39, 1410]	$CaCO_3$
C 6.s	Carbonate, sodium	[21, 1409]	Na_2CO_3
C 7.s	Chlorate, potassium		$KClO_3$
C 8.s	Chloride, sodium (1)	[24, 1411]	$NaCl$
C 9	Chromate, potassium		$K_2Cr_2O_7$
C 10.s	Cyanide, potassium (2)	[45, 1410]	KCN
F 11	Ferricyanide, potassium (2)	[15, 1409]	K_3FeCy_6
F 12	Ferrocyanide, potassium		$K_4FeCy_6.3H_2O$
F 13	Fluoride, calcium (fluorspar)		CaF_2
F 14	Fluosilicic acid	[6, 1410]	H_2SiF_6
H 15	Hypochlorite, sodium (3)		Na_2Cl_2O
I 16	Iodide, potassium		KI
N 17.s	Nitrate, potassium		KNO_3
N 18	Nitrate, lead		$Pb(NO_3)_2$
N 19	Nitrite, potassium	[51, 1410]	KNO_2
O 20	Oxalate, ammonium	[9, 1409]	$(NH_4)_2C_2O_4.2H_2O$
P 21	Phosphate, sodium		$Na_2HPO_4.12H_2O$
S 22	Silicate, sodium (4)		Na_2SiO_3
S 23	Silica, white sand		SiO_2
S 24	Sulphate, sodium		$Na_2SO_4.10H_2O$
S 25	Sulphide, ammonium	[7, 1409]	$(NH_4)_2S$
S 26	Sulphide, ferrous		FeS
S 27.s	Sulphite, sodium		$NaHSO_3$
T 28.s	Tartaric acid	[9, 1410]	$H_2C_4H_4O_6$
T 29	Tartrate, sodium (5)		$Na_2C_4H_4O_6.2H_2O$
T 30	Thiocyanate, potassium	[52, 1410]	$KCNS$
T 31	Thiosulphate, sodium		$Na_2S_2O_3.5H_2O$

REACTIONS OF THE ACID-RADICLES.

with the number, name, formula and normality-strength (1385) of the solution.
in a 4 oz. (120 c.c.) wide-mouthed bottle similarly labelled. Many solutions in this
in column 2: these may be used if necessary from the bottles indicated by the
there is sufficient shelf-room in the laboratory. The acid-radicle portion of the
being inverted, in order to arrange the acid-radicles alphabetically.

Reference Number.	4. Condition, and strength in normality (N) (1385).	5. Grams dissolved to one litre	6. Remarks. [The numbers refer to corresponding small numbers in brackets, column 2.]
A 1	N	65	1. The solution 24, 1411, may be used after dilution with its own volume of water.
A 2	N/5	27	
B 3	In powder	—	2. A small piece of the solid should be dissolved in water immediately before use.
B 4	N/2	52	
C 5	In small pieces	—	3. Strong "liquor sodae chlorinatae" may be diluted with its own volume of water.
C 6	In powder	—	
C 7	N/5	24	4. 30 grams of the syrupy commercial "soluble glass" are dissolved in water, and diluted to a litre with water.
C 8	N/2	29	
C 9	N	49	
C 10	N/2	38	
F 11	In small pieces	—	5. 50 grams of tartaric acid are dissolved in 250 c.c. of water; the hot solution is exactly neutralized by stirring in sodium carbonate, and the solution is diluted to one litre. A suitable solution may be more readily prepared by dissolving 100 grams of "Rochelle salt," $KNa\bar{T}.4H_2O$, in a litre of water
F 12	N	106	
F 13	In powder	—	
F 14	...	—	
H 15	.	—	
I 16	N/10	17	
N 17	N	101	
N 18	In fine powder	—	
N 19	N	85	
O 20	N	80	
P 21	N/5	24	
S 22	...	—	
S 23	In fine powder	—	
S 24	N/5	32	
S 25	.	—	
S 26	In pea-sized pieces	—	
S 27	N	52	
T 28	In small pieces	—	
T 29	.	—	
T 30	N	97	
T 31	N	124	

1413. SPECIAL TEST SUBSTANCES AND REAGENTS FOR THE RARER METALS AND ACID-RADICLES.

I. METALS.

Group I :—	
Thallium sulphate	Tl_2SO_4
Tungstate	Na_2WO_4
Group II :—	
Palladium chloride	$PdCl_2$
Gold chloride [30, 1410]	$AuCl_3$
Platinum chloride [43, 1410]	H_2PtCl_6
Iridium chloride	Na_2IrCl_6
Molybdate	Am_2MoO_4
Selenide	$PbSe$
Selenate	K_2SeO_4
Telluride	$PbTe$
Tellurate	K_2TeO_4
Group III :—	
Beryllium sulphate	$BeSO_4$
Titanium sulphate	$Ti(SO_4)_2$
Cerium nitrate	$Ce(NO_3)_3$
Lanthanum nitrate	$La(NO_3)_3$
Zirconium sulphate	$Zr(SO_4)_2$
Thorium sulphate	$Th(SO_4)_2$
Yttrium nitrate	$Yt(NO_3)_3$
Indium sulphate	$In_2(SO_4)_3$
Uranyl nitrate	$UO_2(NO_3)_2$
Vanadate	$NaVO_3$
Group V :—	
Lithium chloride	$LiCl$
Rubidium chloride	$RbCl$
Caesium chloride	$CsCl$

II. ACID-RADICLES.

Group III :—	
Bromate	$KBrO_3$
Iodate	KIO_3
Group V :—	
Pyrophosphate	$Na_4P_2O_7$
Metaphosphate	$NaPO_3$
Hypophosphite	$NaPH_2O_2$
Group VI :—	
Permanganate	$KMnO_4$
Manganate	K_2MnO_4
Persulphate	$Am_2S_2O_8$
Perchlorate	$KClO_4$
Periodate	$Na_2H_3IO_6$
Percarbonate	$K_2C_2O_6$
Perborate	$NaBO_3.4H_2O$
Hydrogen peroxide	H_2O_2

III. REAGENTS.

Mercuric cyanide solution	$HgCy_2$
Potassium bicarbonate solution	$KHCO_3$
Tin, granulated	Sn
Hydrogen peroxide, dilute acid solution	H_2O_2
Calcium sulphate, fine powder	$CaSO_4$

1414. TEST SUBSTANCES AND REAGENTS FOR ORGANIC SUBSTANCES.

Reagents already in use for inorganic substances are not included.

ORGANIC SUBSTANCES.

Group I. Cyanogen Acid-radicles :—

Cyanide	KCN
Cyanate	$KCNO$
Thiocyanate	$KCNS$
Ferrocyanide	$K_4FeCy_6.3H_2O$
Ferricyanide	K_3FeCy_6

2. *Aliphatic Acid-radicles :—*

Formate	$NaCHO_2$
Acetate	$NaC_2H_3O_2.3H_2O$
Oxalate	$(NH_4)_2C_2O_4.2H_2O$
Succinate	$(NH_4)_2C_4H_4O_4$
Malate	$H_2C_4H_4O_5$
Tartrate	$KNaC_4H_4O_6$, and $NaHC_4H_4O_6$
Citrate	$Na_3C_6H_5O_7.2H_2O$

3. *Aromatic Acid-radicles :—*

Benzoate	$NH_4C_7H_5O_2$
Salicylate	$NaC_7H_5O_3$
Gallate	$HC_7H_5O_5$
Tannate	$C_{14}H_{10}O_9$
Hippurate	$HC_9H_8NO_3$
Meconate	$H_2C_7H_2O_7.3H_2O$
Urate	$KC_5H_3N_4O_3$

Group II. Hydrocarbons and their Derivatives :—

Turpentine	$C_{10}H_{16}$
Benzene	C_6H_6
Naphthalene	$C_{10}H_8$
Anthracene	$C_{14}H_{10}$
Chloroform	$CHCl_3$
Carbon tetrachloride	CCl_4
Iodoform	CHI_3
Carbon disulphide	CS_2

Group III. Alcohols and Ethers :—

Methyl alcohol	CH_3OH
Ethyl alcohol	C_2H_5OH
Amyl alcohol	$C_5H_{11}OH$
Glycerol	$C_3H_5(OH)_3$
Ethyl ether	$(C_2H_5)_2O$
Ethyl acetate	$C_2H_5.C_2H_3O_2$

Group IV. Phenol and its Derivatives :—

Phenol	$C_6H_5.OH$
Hydroquinone	$C_6H_4(OH)_2$
Pyrogallol	$C_6H_3(OH)_3$
Picric acid	$C_6H_2(NO_2)_3OH$

Group V. Aldehydes and Ketones :—

Formaldehyde (solution)	$H.COH$
Acetaldehyde	$CH_3.COH$
Chloral hydrate	$CCl_3.CH(OH)_2$
Benzaldehyde	$C_6H_5.COH$
Acetone	$CO(CH_3)_2$

Group VI. Carbohydrates :—

Dextrose	$C_6H_{12}O_6$
Levulose	$C_6H_{12}O_6$
Sucrose	$C_{12}H_{22}O_{11}$
Maltose	$C_{12}H_{22}O_{11}.H_2O$
Lactose	$C_{12}H_{22}O_{11}.H_2O$
Cellulose	$(C_6H_{10}O_5)n$
Starch	$(C_6H_{10}O_5)n$
Dextrin	$(C_6H_{10}O_5)n$

Group VII. Glucosides :—

Salicin	$C_{13}H_{18}O_7$
Digitalin	$C_{29}H_{46}O_{12}$
Amygdalin	$C_{20}H_{27}O_{11}N$

Group VIII. Organic bases :—

Aniline	$C_6H_5.NH_2$
Toluidine	$C_6H_4.CH_3.NH_2$
Pyridine	C_5H_5N
Quinoline	C_9H_7N
Acetanilide	$C_6H_5.NH.CO.CH_3$
Phenacetin	$C_6H_5O.C_6H_4.NH.COCH_3$
Antipyrin	$C_{11}H_{12}N_2O$
Urea	$CO(NH_2)_2$

Group IX. Alkaloids :—

Quinine	$C_{20}H_{24}N_2O_2.3H_2O$
Quinidine	$2C_{20}H_{24}N_2O_2.5H_2O$
Cinchonine	$C_{19}H_{23}N_2O$
Morphine	$C_{17}H_{19}NO_3$
Apomorphine	$C_{17}H_{17}NO_2$
Codeine	$C_{17}H_{17}NO.OCH_3.OH$
Narcotine	$C_{22}H_{23}NO_7$
Papaverine	$C_{20}H_{21}NO_4$
Strychnine	$C_{21}H_{22}N_2O_2$
Brucine	$C_{23}H_{26}N_2O_4.4H_2O$
Caffeine, Theine	$C_8H_{10}N_4O_2.H_2O$
Cocaine	$C_{17}H_{21}NO_4$
Veratrine	$C_{32}H_{42}NO_9$
Atropine	$C_{17}H_{23}NO_3$
Hyoscyamine	$C_{17}H_{23}NO_3$
Hyoscine	$C_{17}H_{21}NO_4$
Nicotine	$C_{10}H_{14}N_2$
Coniine	$C_8H_{17}N$

REAGENTS.

Sodium picrate, saturated solution	—
Mercuric nitrate, neutral solution	$Hg(NO_3)_2$
Quicklime, in powder	CaO
Potassium bicarbonate solution	$KHCO_3$
Iodic acid, solution (1 : 15)	HIO_3
Iodine, in small fragments	—
Yeast	—
Rochelle salt	$KNa\bar{T}.4H_2O$
Rosaniline (Fuchsine)	—
Zinc chloride	$ZnCl_2$
Ammonium iodide	NH_4I
Sodium nitroprusside	—

SUBSTANCES TO BE GIVEN FOR ANALYSIS BY THE PRECEDING TABLES.

It must be understood that the substances mentioned below are merely brought forward as examples of what may be given to the student for analysis. The teacher will use his own judgment in adopting and extending the list.

SUBSTANCES FOR ANALYSIS WHILE TRYING THROUGH THE REACTIONS FOR METALS AND ACID-RADICLES.

1415. After working through the reactions for a Group of Metals or Acid-radicles, a few unknown substances containing only *one* member of the Group are tested; the number of members present is then gradually increased in the substances which are subsequently given.

It is well to keep these substances in the dissolved state (1411, 1412), since they are intended mainly to afford practice in separation and detection according to the Group-tables; the time spent by the student in preparing the solution would therefore be wasted.

Occasionally, however, a solid substance may be given, in which the Metal or Acid-radicle present is to be detected by blowpipe tests, or by other tests made on the solid substance. The following will serve as examples of solids:—

Group V.	*Group IV.*	*Group III.b.*
Solution of $NaCl$	Solution of $BaCl_2.2H_2O$	Solution of $ZnSO_4.7H_2O$
" " NH_4Cl	" " $Sr(NO_3)_2.4H_2O$	" " $MnCl_2$
" " KCl	" " $CaCl_2.6H_2O$	" " $NiSO_4.7H_2O$
" " $NaCl+KCl$	" " $Sr(NO_3)_2.4H_2O+CaCl_2.6H_2O$	" " $Co(NO_3)_2.6H_2O$
" " $NaCl+NH_4Cl+KCl$	" " $BaCl_2.2H_2O+Sr(NO_3)_2.4H_2O+CaCl_2.6H_2O$	" " $MnCl_2+ZnSO_4.7H_2O$
" " $NaCl+NH_4Cl$	" " $BaCl_2.2H_2O+Sr(NO_3)_2.4H_2O$	" " $Co(NO_3)_2.6H_2O+NiSO_4.7H_2O+ZnSO_4.7H_2O$
" " $MgSO_4.7H_2O+NaCl+KCl$		etc., etc., etc.
Solids: $NaCl$, NH_4Cl, KCl, $AmCl+NaCl$, etc.		*Solids:* $MnCl_2$, $NiSO_4.7H_2O$, $Co(NO_3)_2.6H_2O$. $ZnSO_4.7H_2O$, etc.

SIMPLE SUBSTANCES FOR ANALYSIS.

1416. Any one of the solutions named in paragraphs 1411, 1412 may be given for analysis: some of these are neutral, some acid, and others alkaline in reaction. The following more difficult solutions, with acid or alkaline reaction, may also be added to the list:—

Acid.	*Alkaline.*
$Ca_3(PO_4)_2$, "Bone-ash" dissolved in dilute HCl.	$KSbO_3$ dissolved in water.
BaC_2O_4 dissolved in dilute HCl.	Na_2SiO_3, solution of "soluble glass."
$Mg(BO_2)_2$* " " HCl.	Na_2SnO_3, "preparing salt" of the dyer.
$BaCrO_4$ " " HCl.	

*Made by mixing hot solutions of $Na_2B_4O_7$ and $Mg(NO_3)$.

As examples of substances possessing metallic appearance (1299), the following may be mentioned as suitable for analysis :—

Zn, in pieces or filings. Pb ,, ,, FeS_2, Iron pyrites.	NiAs, Copper-nickel. Graphite, or Black lead. Iron filings.

As insoluble substances which require to be examined by paragraphs 1306, *et seq.*, the following may be given for analysis :—

$BaSO_4$. $PbSO_4$. AgCl. SnO_2, Tinstone.	CaF_2, Fluor spar. $FeCr_2O_4$, Chrome Iron ore. S, as pieces of roll sulphur. C, as powdered wood charcoal or plumbago.

SOLID SUBSTANCES TO BE ANALYSED BY THE PRELIMINARY EXAMINATION IN SECTION VI.

1417. For the Preliminary Examination for Metals (1215–1224) :—

Simple.			*Complex.*	
NH_4Cl $HgCl_2$ As_4O_6 KNO_3 Cr_2O_3	$Pb(NO_3)_2$ NaCl $BaCl_2.2H_2O$ $Sr(NO_3)_2.4H_2O$ $CuSO_4.5H_2O$ (See *Note.*)	$ZnSO_4.7H_2O$ $MnCl_2$ $Co(NO_3)_2.6H_2O$ $NiSO_4.7H_2O$ SnO_2	AmCl+NaCl $HgCl_2+BaCl_2.2H_2O$ $MnCl_2+KCl$ $NiSO_4.7H_2O+$ $ZnSO_4.7H_2O$	$AlK(SO_4)_2.12H_2O$ $SnO_2+Sr(NO_3)_2.4H_2O$ $CaCO_3+ZnSO_4.7H_2O$ $Cr_2O_3+MnCl_2+$ NaCl

Note.—Best finely powdered, since its colour is then almost destroyed.

For the Preliminary Examination for Acid-radicles (1225–1228) :—

Simple.			*Complex.*
$CaCO_3$ $Na_2SO_3.7H_2O$ $CaCl_2O$ NaCl	FeS KNO_3 $KClO_3$ KI	$Na_2S_2O_3.5H_2O$ KBr $Na\bar{A}$	$CaCO_3+KNO_3$ $CaCl_2O+CaF_2$ Na_2CO_3+KI

A few of the above-mentioned solids may then be examined by both Preliminary Examinations for Metals and for Acid-radicles.

SUBSTANCES TO BE ANALYSED BY THE GENERAL COURSE IN SECTION VI.

1418. The following lists are so arranged that the analysis of the substances contained in them is more difficult in each column proceeding from left to right, and usually from top to bottom in one and the same column. For examples of alkaline solutions, see paragraph 1416.

1. Simple soluble substances.	2. Complex soluble substances.	3. Complex soluble substances.
$BaCl_2.2H_2O$ $MnCl_2$ $HgCl_2$	$CaCl_2.6H_2O+BaCl_2.2H_2O+Sr(NO_3)_2.4H_2O$ $AlK(SO_4)_2.12H_2O+CrK(SO_4)_2.12H_2O$ $MnCl_2+ZnSO_4.7H_2O+CuSO_4.5H_2O$	{ $FeCl_3$ $MnCl_2$ $ZnSO_4.7H_2O$ KCl }
$MgSO_4.7H_2O$ KCl $NiSO_4.7H_2O$	$Pb(NO_3)_2+HgCl_2+NaCl$ *$As_4O_6+CaCO_3+BaCO_3$ *$ZnO+MgCO_3+KClO_3$	{ As_4O_6 $CrK(SO_4)_2.12H_2O$ $Co(NO_3)_2.6H_2O$ }
*$CaCO_3$ $Pb(NO_3)_2$ *As_4O_6 $FeCl_3$ NH_4Cl $NaCl$ etc., etc.	*$MgCO_3+BaCO_3+PbCO_3$ etc., etc.	{ $Hg_2(NO_3)_2.H_2O$ $Sr(NO_3)_2.4H_2O$ KNO_3 $Bi(NO_3)_3.5H_2O$ } etc., etc.

* To be given in the solid state.

4. Substances yielding a Phosphate-precipitate in Group III.	5. Substances partly or entirely insoluble.	
{ $CaCl_2.6H_2O$ $FeCl_3$ $Na_2HPO_4.12H_2O$ }	$BaSO_4$ SiO_2+S $BaSO_4+CaF_2+SnO_2$	*Metallic substances* (1299–1305):— Iron pyrites (FeS_2) Iron filings (Fe) Zinc clippings (Zn) Brass filings (Cu+Zn) Nickel silver (Cu+Zn+Ni) Bronze (Cu+Sn) Type-metal (Sb+Sn+Pb) Aluminium bronze (Cu+Al)
{ $BaCl_2.2H_2O$ $MgCl_2$ $FeCl_3$ $Na_2HPO_4.12H_2O$ }	{ $BaCl_2.2H_2O$ $AlK(SO_4)_2.12H_2O$ $AgNO_3$ }	*Silicates* (1312–1315):— Kaolin ($Al_2O_3.2SiO_2$) Brown-clay (do. +Fe) Window-glass (Na, Ca, SiO_2) Flint-glass (Pb, K, SiO_2)
{ $Co(NO_3)_2.6H_2O$ $CaCl_2.6H_2O$ $MnCl_2$ $CrK(SO_4)_2.12H_2O$ $Na_2HPO_4.12H_2O$ } etc., etc.	{ SiO_2 S C } $PbSO_4+BaSO_4$ $PbCrO_4$, ignited.	*Cyanogen Compounds* (1316-1322):—Any of the foregoing which has been mixed with KCN, KCNS, $K_4FeCy_6.3H_2O$, K_3FeCy_6, K_3CoCy_6

MINERALS FOR ANALYSIS

1419. The minerals are ranged under one of the principal metals which they contain, and these metals are placed in the order in which they occur in the Analytical Reactions (101–448). The names of minerals which contain the less common metals will usually be found above the reactions of each of those metals. In this list only the more common natural compounds are included, and the traces of impurities which they may contain are not specified in stating their composition by formulae.

GROUP I.—SILVER GROUP.

Lead :—

Galena, PbS.
Cerussite, $PbCO_3$.
Anglesite, $PbSO_4$.
Leadhillite, $PbSO_4.3PbCO_3$.
Pyromorphite, $3Pb_3(PO_4)_2.PbCl_2$.
Crocoisite, $PbCrO_4$.

Silver :—

Native silver, Ag.
Horn silver, $AgCl$.
Silver glance, or Argentite, Ag_2S.
Pyrargyrite, Ag_3SbS_3.
Proustite, Ag_3AsS_3.

GROUP II.A.—COPPER GROUP

Mercury :—

Cinnabar, HgS.

Bismuth :—

Native bismuth, Bi.
Bismuth ochre, Bi_2O_3.
Bismuthine, or Bismuth glance, Bi_2S_3.
Complex bismuth sulphides.

Copper :—

Native copper, Cu.
Cuprite, or Red copper ore, Cu_2O.
Copper glance, Cu_2S.
Copper pyrites, or Peacock copper ore, $CuFeS_2$.
Ernbescite, or Bornite, Cu_3FeS_3.
Tetrahedrite, $4Cu_2S.Sb_2S_3$.
Malachite, $CuCO_3.Cu(OH)_2$.
Azurite, or Chessylite, $2CuCO_3.Cu(OH)_2$.

Cadmium :—

Greenockite, CdS.

GROUP II.B.—ARSENIC GROUP.

Arsenic :—

Native arsenic, As.
Realgar, As_2S_2.
Orpiment, As_2S_3.
Mispickel, FeAsS.
Copper-nickel, NiAs.
Arsenical nickel, $NiAs_2$.
Arsenosulphides.

Antimony :—

Native antimony, Sb.
Stibnite, or Grey antimony, Sb_2S_3.
Complex antimony sulphides.
White antimony ore, Sb_2O_3.
Red antimony ore, $Sb_2O_3.2Sb_2S_3$.

Tin :—

Tinstone, or Cassiterite, SnO_2.
Stannite, or Tin pyrites, Cu_2FeSnS_4.

GROUP III.A.—IRON GROUP.

Aluminium :—

Corundum, Al_2O_3.
Bauxite, $Al_2O_3(Fe_2O_3).2H_2O$.
Diaspore, $Al_2O_3.H_2O$.
Alumstone, $K_2O.3Al_2O_3.4SO_3.6H_2O$.
Cryolite, $AlF_3.3NaF$.
Felspar (see K and Na).
Clay, $Al_2Si_2O_7.2H_2O$.

Iron :—

Meteoric iron, Fe + Ni.
Red haematite, or Specular iron ore, Fe_2O_3.
Brown haematite, or Limonite, $2Fe_2O_3.3H_2O$.
Magnetite, or Magnetic iron ore, Fe_3O_4.
Iron pyrites, FeS_2.
Pyrrhotite, or Magnetic pyrites, $Fe_{11}S_{12}$.
Chalybite, or Spathic iron ore, $FeCO_3$.
Clay ironstone, $FeCO_3$ + clay.
Black-band ironstone, $FeCO_3$ + bitumen.

Chromium :—

Chromite, or Chrome ironstone, $FeCr_2O_4$.
Crocoisite, $PbCrO_4$.

GROUP III.B.—ZINC GROUP.

Zinc :—

Zincite, or Red zinc ore, ZnO.
Zinc blende, ZnS.
Calamine, $ZnCO_3$.
Silicious (electric) calamine, or Hemimorphite, $2ZnSiO_4.H_2O$.
Franklinite, $(Zn,Fe)O.Fe_2O_3$.

Manganese :—

Pyrolusite, MnO_2.
Braunite, Mn_2O_3.
Hausmannite, Mn_3O_4.
Manganite, $Mn_2H_2O_4$.
Psilomelane, $(Mn,Ba)O.MnO_2$.
Wad, mainly hydrated MnO_2 and Mn_2O_3.
Dialogite, or Manganese spar, $MnCO_3$.

Nickel :—

Copper-nickel, NiAs.
Chloanthite, $NiAs_2$.
Garnierite, Hydrated Ni,Mg silicates.

Cobalt :—

Smaltite, $CoAs_2$.
Cobaltite, CoAsS.

GROUP IV.—BARIUM GROUP.

Barium :—

Barytes, or Heavy spar, $BaSO_4$.
Witherite, $BaCO_3$.

Strontium :—

Celestine, $SrSO_4$.
Strontianite, $SrCO_3$.

Calcium :—

Calcite or Calcspar, Arragonite, Marble, Chalk, Limestone, $CaCO_3$.
Dolomite, or Magnesian limestone, $(Ca,Mg)CO_3$.
Gypsum, Selenite, or Alabaster, $CaSO_4.2H_2O$.
Anhydrite, $CaSO_4$.
Fluorspar, CaF_2,
Fluor-apatite, $3Ca_3(PO_4)_2.CaF_2$.
Chlor-apatite, $3Ca_3(PO_4)_2.CaCl_2$.

GROUP V.—POTASSIUM AND MAGNESIUM GROUP.

Potassium :—

Nitre, or Saltpetre, KNO_3.
Sylvine, KCl.
Kainite (see Magnesium).
Carnallite, $KCl.MgCl_2.6H_2O$.
Alumstone, $K_2O.3Al_2O_3.4SO_3.6H_2O$.
Orthoclase (Potash) Felspar, $K_2O.Al_2O_3.6SiO_2$.

Sodium :—

Rocksalt, NaCl.
Natron, or Native soda, $Na_2CO_3.10H_2O$.
Trona, $Na_2CO_3.NaHCO_3.3H_2O$.
Soda nitre, or Chili saltpetre, $NaNO_3$.
Glauber salt, $Na_2SO_4.10H_2O$.
Glauberite, $Na_2SO_4.CaSO_4$.
Cryolite, $AlF_3.3NaF$.
Albite (Soda) Felspar, $Na_2O.Al_2O_3.6SiO_2$.
Borax, or Tincal, $Na_2B_4O_7.10H_2O$.

Magnesium :—

Periclase, MgO.
Brucite, $MgO.H_2O$.
Magnesite, $MgCO_3$.
Dolomite, or Magnesian limestone, $(Mg,Ca)CO_3$.
Spinel, $MgO.Al_2O_3$.
Kainite, $MgSO_4.KCl.3H_2O$.
Kieserite, $MgSO_4.H_2O$.
Epsomite, $MgSO_4.7H_2O$.
Boracite, $6MgO.MgCl_2.8B_2O_3$.
Meerschaum, $Mg_2H_23SiO_2.H_2O$.

Silica :—

Quartz, Rock crystal, Flint, SiO_2.

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